# SOLID ACID CATALYST FOR SELECTIVE SYNTHESIS OF 2-PHENYLDODECANE

BY

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This thesis is dedicated to our beloved Prophet Muhammad (PBUH)

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# LIST OF ABBREVIATIONS

$C_i$ concentration of specie *i* (mol/$m^3$)

CL confidence limit

$E_i$ apparent activation energy of the *i*th reaction (kJ/mol)

$k_i$ apparent rate constant for the *i*th reaction ($m^3$/kg of catalyst.s)

$k_{oi}$ pre-exponential factor for the *i*th reaction after re-parameterization ($m^3$/kg of catalyst .s)

$M_{Wi}$ molecular weight of specie *i*

$F_{d0}$ Molar flow rate of 1-dodecene into the reactor

$F_d$ Molar flow rate of 1-dodecene leaving the reactor

$F_{LAB}$ Molar flow rate of linear alkylbenzene isomers leaving the reactor

$F_{2\text{-}PD}$ Molar flow rate of 2-phenyldodecane leaving the reactor

$F_t$ Total molar flow rate

*R* universal gas constant (J/mol K)

*T* reaction temperature (K)

$T_o$ reference temperature for the parameter estimation

B Benzene

DD Dodecene

DD2 2-Dodecene

DD3 3-Dodecene

PD2 2-phenyldodecane

PD3 3-phenyldodecane

LAB Linear alkylbenzene

LABS Linear alkylbenzene sulphonates

MOR Mordenites

BEA Beta zeolites

FAU USY zeolites

**Greek Letters**

$\rho$ density of species

$\tau$ space time (min.)

# ABSTRACT

Full Name : Waqas Aslam

Thesis Title : Solid acid catalyst for selective synthesis of 2-phenyldodecane.

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The alkylation of benzene with 1-dodecene to linear alkylbenzenes (LAB) was investigated over 12 membered ring zeolites MOR, BEA, and FAU with varying framework topologies and $SiO_2/Al_2O_3$ ratios. The reaction was carried out under a high-pressure, 20 bar, in a fixed-bed flow reactor at 140◦C, using WHSV 4 h−1, benzene/1-dodecene molar ratio of 6.0 and time-on-stream of 6.0 h. In contrast to MOR and BEA zeolites, FAU exhibited the lowest selectivity (24%) to the desired 2-phenyl dodecane (2-LAB) due to its large cavities. The MOR and BEA with different $SiO_2/Al_2O_3$ ratios were further desilicated using alkali-metal treatments (0.2 M and 0.05 M NaOH) to create hierarchical porous structure. The desilication of both zeolites improved the conversion of 1-dodecene and the selectivity to 2-LAB. The excellent stability resulting from desilication is attributed to a better diffusivity of the LAB isomers, shortening of real contact time, due to the enhanced mesporous structure in both zeolites and the higher Lewis acidity. The selectivity to 2-LAB increased to70% over desilicated MOR ($SiO_2/Al_2O_3$ ratio = 20) compared with a selectivity of 35% over desilicated BEA ($SiO_2/Al_2O_3$ ratio = 24).

Based on the excellent catalytic performance, a detailed kinetic model was developed for alkylation of benzene with dodecene over mordenite ($SiO_2/Al_2O_3$ ratio = 20). The kinetic experiments were conducted in a fixed bed reactor with 6:1 molar ratio

of benzene to dodecene at four different temperature levels between 80 to 140 °C. The product analysis showed that the main alkylation product is 2-phenyldodecane. At lower temperature, the concentration of dodecene isomers was significant. However, at higher temperatures the reaction products mainly comprised of linear alkylbenzene isomers. The kinetic models were formulated considering simultaneous dodecene isomerization and benzene alkylation. The kinetic parameters are estimated by fitting of the experimental data in the MATLAB. The adequacy of the estimated model parameters were verified by thermodynamic consistency and statistical fitting indicators. The activation energy for protonation of 1-dodecene to 2-dodecene was found to be significantly lower (34 kJ/mol) than that of the 2-dodecene to 3-dodecene reaction (51 kJ/mol). The activation energies of surface alkylation of benzene to 2-phenyldodecane and 3-phenyldodecane were 49 kJ/mol and 66 kJ/mol, respectively.

# ARABIC ABSTRACT

# ملخص الرسالة

**الاسم الكامل:** وقاص أسلم

**عنوان الرسالة: الحفّاز الحمضي الصلب للتركيب الاختياري لمادة 2-فينيلدوديكان**

**التخصص: الهندسة الكيميائية**

**تاريخ الدرجة العلمية:** نوفمبر ٢٠١٣

تمت دراسة عملية ألكنة البنزين لإنتاج ألكيل البنزين الخطي (LAB) باستعمال عوامل حفازة حمضية مختلفة التشكيل البنائي (MOR, BEA, FAU) ومختلف نسبة السيليكا الى الألومينا ( $SiO_2/Al_2O_3$). تم اجراء التفاعل في مفاعل من النوع (fixed-bed flow reactor) تحت ضغط عالي(20 bar) ,درجة حرارة (140◦C) ونسبة المتفاعلات المدخلة الى المفاعل (benzene/1-dodecene) تساوي 6.0, و مدة التفاعل 6 ساعات.

على النقيض من الحفازات ( MORوBEA ) فإن الحفاز(FAU) أظهر انتقائية قليلة تجاه المنتج ( 2-phenyl dodecane) وذلك بسبب مساماته الكبيرة. تمت تغير نسبة السيليكا للألومنيوم للحصول على تشكيل مسامي هرمي عن طريق معالجة الحفازات باستخدام هيدروكسيدات قلوي ة(NaOH) بتراكيز مختلفة ( 0.2 و0.05 ) مولار . تقليل نسبة السيليكا للألمونيوم هذه أدت الى تحسين نسبة تحويل المتفاعلات (conversion) والانتقائية اتجاه المنتج المرغوب(2-LAB). يمكن تعليل هذه التحسينات بأن عملية إزالة جزء من السيليكا المكونة للحفاز تؤدي إلى تسهيل حركة المتفاعلات داخل الحفاز وذلك بسبب المسامات الواسعة التي نتجت من إزالة السيليكا إضافة إلى أن هناللك تقليل مصاحب لنسبة الحمضية العالية ( higher Lewis acidity) . نتيجة لذلك فإن الانتقائية زادت إلى نسبة (70%) .

أجريت دراسة كيناتيكية التفاعلات لعملية ألكنة البنزين لإنتاج ألكيل البنزين الخطي (LAB), تم إجراء التفاعلات بنفس كيفية التجارب السابقة باستثناء أن التفاعل تم إجراؤه عند درجات حرارة مختلفة (80 to 140 °C).

من خلال تحليل النتائج المتحصل عليها تم استنتاج أن المنتج الأساسي هو (2-phenyldodecane). عند درجات الحرارة المنخفضة فإن نسبة تحويل المتفاعلات تكون عالية ولكن عند درجات الحراة العالية يكون المنتج الأساسي هو ألكيل البنزين الخطي (LAB).

تمت صياغة نموذج التفاعلي الكيناتيكي باعتبار التوالي في حصول تفاعل الأيزوميريزيشن للدوديكان و تفاعل الألكلة للبنزين. تم تحديد قيم المعاملات الكيناتيكية بعمل مناسبة للنتائج التجريبية باستخدام برنامج MATLAB. تم التأكد من صحة المعاملات التي تم تحديدها عن طريق مؤشرات المناسبة الإحصائية و التناسب الديناميكي الحراري.

تم إيجاد طاقة التنشيط لتحويل 1-دوديكان إلى2-دوديكان و التي كانت 34 كيلوجول/مول و هي أقل من تحويل 2-دوديكان إلى 3-دوديكان بطاقة تنشيط 51 كيلوجول /مول . أما طاقة التنشيط لتفاعل الألكلة السطحي للبنزين إلى 2- فينيلدوديكان و 3- فينيلدوديكان فكانت 49كيلوجول /مول للأول و 66كيلوجول /مول للثاني .

# CHAPTER 1

# INTRODUCTION

Linear alkylbenzene (LAB) are important intermediates used in the detergency sector. The industrial process for LAB production is based on alkylation of benzene with olefins using highly corrosive and dangerous Lewis and Bronsted acids such as aluminum trichloride ($AlCl_3$) and hydrofluoric acid (HF) [1]. The final isomer distribution in the product LAB strongly depends on the nature and distribution of acidity (Brønsted or Lewis) and amount of catalyst, solvent, temperature and the position of the double bond in the starting olefin. Position of the phenyl group and the alkyl chain length in LAB are important factors in determining their surface active properties and biodegradability. Since this process generates a substantial amount of waste, is corrosive, costly and unsafe, there exists a tremendous scope to replace these catalysts with environmentally safer solid acids which can be recovered and reused [2].

Linear alkylbenzenes (LAB) are sulphonated to produce Linear alkylbenzene sulphonates (LABS), containing different carbon atoms in the alkyl chain, are the most important biodegradable surfactants that are used in formulations of light-duty ($C_{11}$-$C_{12}$) and heavy-duty ($C_{12}$-$C_{14}$) detergents, lubricants ($C_{16}$-$C_{24}$), and surfactant flooding ($C_{16}$) in tertiary oil recovery. The increasing use of detergents causes further release and accumulation of LABS and its derivatives in rivers and streams. Rapid biodegradation of the released organic compounds is highly desired to keep the pollutant as low as possible.

Among LAB isomers, particularly 2-phenylalkane or 2-phenylalkane sulfonate is the most readily biodegradable and environmental favorable isomer [2].

## 1.1 Historical background

Natural soaps are sodium salts of fatty acids obtained by alkaline saponification of triglycerides from either vegetable or animal sources. These natural soaps were prevalent until the 1940s when sodium alkylbenzene sulfonates became available. These synthetic surfactants had detergency characteristics that were superior to those of natural soaps. Additionally, the synthetic surfactants had a lower cost and a wider range of applications. This new surfactant replaced natural soaps in household laundry and dishwashing applications. The discovery of synthetic alkylbenzene sulfonates formed the basis for the detergent industry. The first alkylbenzene sulfonates were obtained by the Friedel–Crafts alkylation of benzene with propylene tetramer. The tetramer is a mixture of $C_{12}$ olefins. As a result, the corresponding alkylbenzene sulfonate is highly branched. The detergent product is then made by sulfonation of the dodecylbenzenes with oleum or sulfur trioxide followed by neutralization with sodium hydroxide or soda ash. The active-detergent could then be formulated into the commercial product [3]. Although the dodecylbenzene was an effective detergent, it has slow rates of biodegradation in the environment. It became apparent that dodecylbenzene based detergents were contributing to the pollution of lakes and streams by forming relatively stable foams. In the early 1960s, the linear alkylbenzene sulfonates were introduced. Due to its superior biodegradability, linear alkylbenezene sulfonates began replacing branched dodecylbenzene sulfonates. Dodecylbenzene sulfonate was largely replaced by linear alkylbenzene sulfonate by the late 1960s in the United States, Japan, and many European countries. Furthermore, by the

late 1970s, linear alkylbenzene sulfonate capacity increased rapidly with facilities being installed around the world [3].

## 1.2 Demand of linear alkylbenzene

With nearly 3.7 million tons/year of global capacity, linear and branched alkylbenzenes are key surfactant intermediates. With the use of branched alkylbenzene declining rapidly since 2004, technical applications have become the main market for branched alkylbenzene sulfonates. Linear alkylbenzene consumption has benefitted from the decline of branched, as well as from a strong position relative to alcohol derivatives. With rising fats and oil prices disrupting the launch of nearly a million tons of new alcohol capacity due for start-up in 2007-2008, the competitive positioning of detergent alkylates has shifted favorably.

According to a study, DETERGENT ALKYLATES – WORLD MARKET, 2006-20016, carried out by COLIN A. HOUSTON ASSOCIATES, INC., the shift in Regional Consumption of LAB from year 1999 to year 2010 was predicted to be as follows:

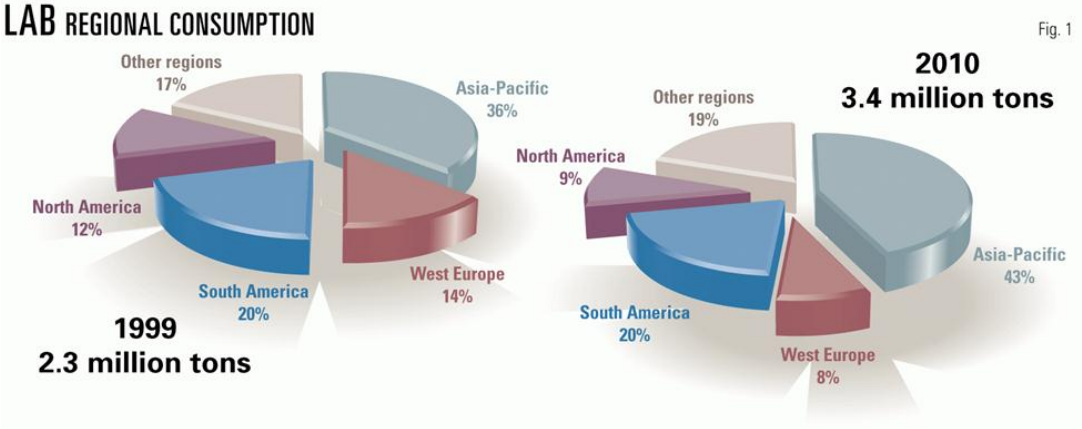



Figure 1: Consumption of LAB across the globe [4]

The study reveals that:

- Global consumption of LAB **increased** at a rate of **3.6% per year** from the period 1999 to 2010, whereas that of branched alkylbenzene (BAB) derivatives **decreased** at a rate of **8% per year**, in the same period.

- In the year 1999, LAB accounted for **92%** of Detergent Alkylate market, by 2010 its share raise to **98%**.

- The regional growth in linear alkylbenzene demand from the year 1999 to 2010 raise at the following rate:

Table 1: Growth in demand of LAB [4]

| **Region** | **LAB demand growth per year** |
|---|---|
| Asia Pacific | 5.1 % |
| Latin America | 3.5% |
| North America | 1% |
| West Europe | 1.2% (decline) |
| Middle East & Africa | 4.6% |

- Global demand of LAB will grow at **2.5% per year** through 2016.

By 2007, Global linear alkylbenzene production capacity was approx. 3.7 million tons/year. According to the study, more than **300,000 tons/year** of additional LAB capacity required after 2010 to bring LAB supply in balance with demand [4].

The increase in demand of LAB across different parts of the world was estimated to increase at CAGR (compound annual growth rate) of 2.7% through the year 2010 to 2015. As predicted by Amandeep Singh [5].

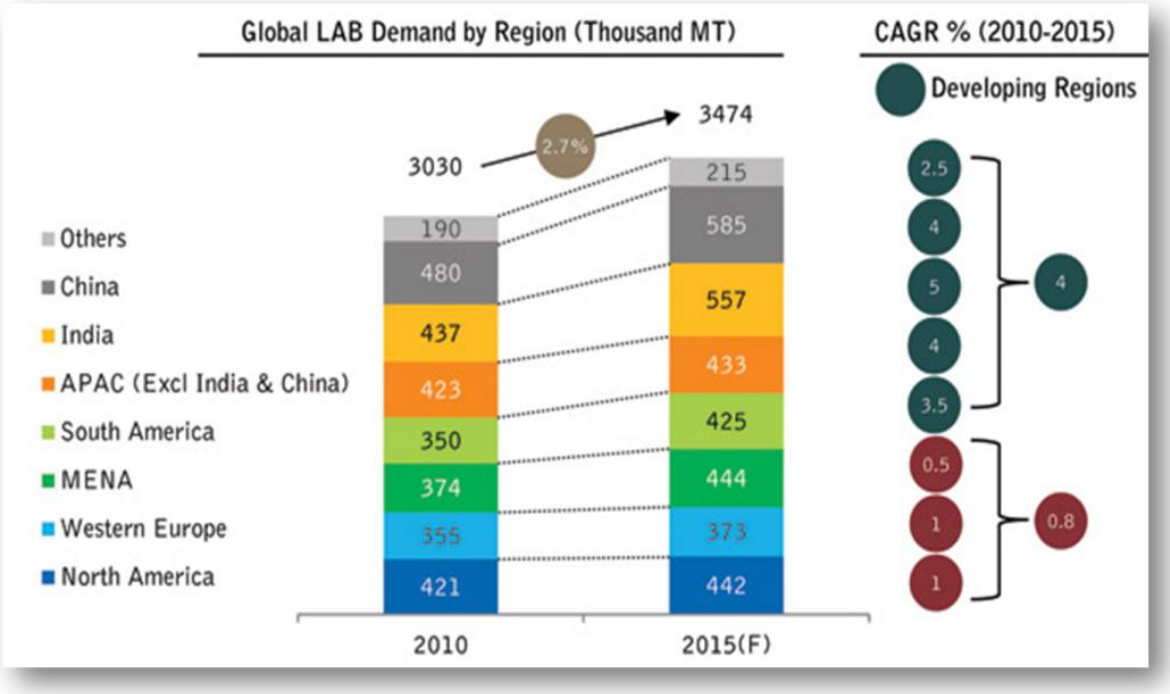



Figure 2: LAB demand across the globe [5]

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Linear alkylbenzene technology overview

The linear paraffins are converted into alkyl chlorides or olefins, and alkylating benzene with them produces linear alkylbenzenes. Various technologies developed include:

• Chlorination of linear paraffins to form monochloroparaffin. Aluminum chloride catalyst is used to alkylate benzene with the mono-chloroparaffin. For example, ARCO Technology Inc. has developed and commercialized this route.

• Chlorination of linear paraffins followed by dehydrochlorination to form olefins as the alkylating agent that has been used by a few companies. Shell's CDC (chlorination/dehydrochlorination) process is an example. Hydrofluoric acid is generally used as the catalyst for benzene alkylation with linear olefins.

• Wax cracking, alpha olefins from ethylene oligomerization, or linear internal olefins from olefin disproportionation can produce olefins. Alkylation of benzene with these olefins is conducted using hydrofluoric acid catalyst. Companies that use these various routes include Albermarle (now Amoco), Chevron, and Shell.

• Dehydrogenation of linear paraffins to a mixture of linear olefins is another route to paraffin activation. The olefin-containing stream is used to alkylate benzene using HF acid catalyst. The unconverted paraffins are then recycled back to dehydrogenation after separation by distillation. UOPs Pacol$^{TM}$ process and UOPs Detergent Alkylate$^{TM}$ process

are examples of this approach. Huntsman Corp. (formerly Monsanto) also practices this approach. The paraffin chlorination route followed by aluminum chloride catalyzed alkylation was used in the early 1960s. The dehydrogenation with hydrofluoric acid alkylation route became more popular in the late 1960s. It became the prominent technology because of higher-quality product and economic advantages. Additionally, the paraffin dehydrogenation routes have in general prevailed because of lower cost of the kerosene feedstock [6]. Table 2 shows the approximate distribution of world linear alkylbenzene production using these technologies.

Table 2: Overview of LAB manufacturing technologies [6]

| **Thousand metric tonnes annually** | **YEAR** | | | |
|---|---|---|---|---|
| | 1970 | 1980 | 1990 | 2000 |
| Chlorination + alkylation | 400 | 400 | 240 | 180 |
| High purity olefins to alkylation | 0 | 100 | 280 | 120 |
| Dehydrogenation + HF alkylation | 260 | 600 | 1280 | 1850 |
| Dehydrogenation + solid-bed alkylation | 0 | 0 | 0 | 260 |
| Total | 660 | 1100 | 1800 | 2410 |

The dehydrogenation followed by alkylation route accounts for 88% of world production. Hydrofluoric acid is an excellent catalyst; however, potential for the accidental release of hydrofluoric acid has raised environmental safety concerns (Clean Air Act, 1990 Amendment). Maximum safety measures are taken at modern HF alkylation complexes,

therefore, the potential of accidental release is minimal. Nonetheless, replacing hydrofluoric acid with a solid catalyst is desired. Recently, a new process using a solid catalyst was developed. The Detal$^{TM}$ process that uses a non-corrosive solid catalyst was commercialized in 1995 [6].

### 2.1.1 Comparison of hydrofluoric acid vs Detal process:

Table 3 compares linear alkylbenzene product properties for the HF and Detal catalyst systems. Bromine index and sulfonatability are key measures of product quality because they affect final product cost.

Table 3: Comparison of HF alkylation vs Detal process [6]

| | **HF linear alkylbenzene** | **Detal linear alkylbenzene** |
|---|---|---|
| Linearity (%) | 92–93 | 94–95 |
| Specific gravity | 0.86 | 0.86 |
| Bromine index | <15 | <15 |
| Saybolt color | >30 | >30 |
| Water (ppm) | <100 | <100 |
| Tetralins (wt.%) | <1.0 | <0.5 |
| 2-Phenylalkanes (wt.%) | 15–18 | >25 |
| n-Alkylbenzene (wt.%) | 93 | 95 |
| Klett color of 5% solution | 20–40 | 10–30 |

High bromine index product also produced a highly colored sulfonate that required further treatment. Recently, reduction in non-alkylbenzene components, in particular

reduction of tetralins and improved linearity are more important. Both of these parameters are related to improved rate of biodegradation of the ultimate product. As can be seen in the Table 3, the Detal linear alkylbenzene product is produced in higher yield, with higher linearity, improved sulphonate color, and less tetralin by-product. It also has higher 2-phenylalkane content that adds improved solubility in many formulations. All of these properties demonstrate that the current Detal technology produces a superior product than the hydrofluoric acid technology [6].

## 2.2 Zeolites

Zeolites occur in nature and have been known for faujasites (zeolites X and Y) on an industrial scale in almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, offretite, ferrierite, chemierionite and chabazite. Today, these and other structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because (i) they almost always contain undesired catalysts (which enabled drastic process engineering impurity phases, (ii) their chemical composition varies from one deposit to another, the most one stratum to another in the same deposit, and (iii) nature did not optimize their properties for catalytic applications [7].

The elementary building units of zeolites are $SiO_4$ and $AlO_4$ tetrahedra. Adjacent tetrahedra are linked at their corners via a common oxygen atom, and this results in an inorganic macromolecule with a structurally distinct three-dimensional framework. It is evident from this building principle that the net formulae of the tetrahedra are **$SiO_2$** and **$A1O_2$,** i.e., one negative charge resides at each tetrahedron in the framework which has aluminum in its center. The framework of a zeolite contains channels, channel

intersections and/or cages with dimensions from 0.2 to 1 nm. Inside these voids are water molecules and small cations which compensate the negative framework charge [7].

Among the unique features of zeolites compared to more conventional solid catalysts or catalyst supports are (i) their strictly uniform pore diameters and (ii) pore widths in the order of molecular dimensions. Bearing in mind the pertinent IUPAC classification for:

**micropores: 2.0 nm >= $d_p$,**

**mesopores: 2.0 nm < $d_p$ < 50 nm and,**

**macropores: $d_p$ > 50 nm**

with $d_p$ being the pore diameter, zeolites are typical microporous materials [7].

### 2.2.1 Acidity of zeolites

Among the most important properties of zeolites with respect to their use as catalysts is their surface acidity. To describe the acidity of zeolites in adequate manner, it is mandatory to clearly distinguish between (i) the nature of the acid sites (i.e., Bronsted vs. Lewis acidity), (ii) the density or concentration of these sites, (iii) their strength or strength distribution and, last but not least, (iv) the precise location of the acid sites.

#### 2.2.1.1 Nature of acid sites

Both Bronsted and Lewis acid sites occur in zeolites. Bronsted acid sites are almost always generated by either of the procedures represented by the following chemical equation, where Z- stands for the negatively charged framework:

$$NH_4^+ + Na^+Z^- \underset{-Na^+}{\rightarrow} NH_4^+Z^- \overset{\approx 300-400^\circ C}{\underset{-NH_3}{\rightarrow}} H^+Z^-$$

i.e., aqueous ion exchange with an ammonium salt followed by thermal decomposition of the ammonium ions inside the zeolite. It has been repeatedly found that the activity stems from the Bronsted rather than Lewis acid sites. It is doubtful whether the Lewis sites play a role at all in acid-catalyzed reactions. It possess the high acid strength of zeolites, and this is has been claimed [7] that, under certain circumstances, Lewis acid sites might enhance the strength of nearby Bronsted sites, thereby exerting an indirect influence on the catalytic activity.

#### 2.2.1.2 Density and strength of acid sites

The density of Bronsted acid sites in a zeolite is obviously related to the framework aluminum content. Limiting cases are pure zeosils, which lack acidity, and aluminum-rich zeolites such as HY. Note that zeolite X which is even richer in aluminum is unstable in the $H^+$-form. The density of Bronsted sites can be measured by, e.g. 'H-NMR spectroscopy or IR spectroscopy, either with or without adsorption of a base like pyridine, but the latter requires the knowledge of reliable extinction co-efficient which are often difficult to find. Similarly, the density of Lewis acid sites is accessible through IR measurements using the 1455 $cm^{-1}$ band adsorption of pyridine (here again reliable extinction coefficients are needed).

The density of Bronsted acid sites in a zeolite will occur on completely isolated $A1O_4$ -tetrahedra, i.e. those which lack $A1O_4$-tetrahedra as next nearest neighbors. This is the reason why, upon dealumination of Y-zeolites with a typical $n_{Si}/n_{A1}$ of 2.5, the catalytic activity generally *increases* up to $n_{si}/n_{Al}$ = **10.** In this region, the gain in acid strength over-compensates the decrease in the density of Bronsted acid sites. From a certain $n_{Si}/n_{Al}$

onwards (and with high-quality zeolite samples) the activity per acid site remains constant [7].

#### 2.2.1.3 Location of the acid sites:

A complete description of zeolite acidity would include a detailed analysis of catalytically active sites. To what extent do these occur on the external surface of the crystals and inside the pores (only the internal surface can be expected to show shape selectivity, vide infra)? To what extent do the sites occur in large cavities, which are accessible for bulky reactant molecules, and in smaller cavities in which they are hidden for such molecules? Are the acid sites evenly distributed over the crystals, or are they concentrated in a shell near the external surface or, conversely, in the core of the crystals? More and more examples for surprising distributions of the location of acid sites are emerging in the literature [7].

### 2.2.2 Zeolites vs amorphous silica-alumina:

Protonic acid sites (Bronsted acid sites) comes essentially from 'Bridged Hydroxyl groups' in the framework. The maximum concentration of protonic acid sites is equal to the concentration of Al atoms in the framework of the zeolite but real concentration is usually lower. Acid sites strength in zeolites is much higher than in amorphous silica-alumina. In zeolite structures Fig. 3, Al-O and Si-O bonds are almost equivalent and the strong interaction Al-O results in a weaker bond O-H increasing the strength of the proton. On the contrary, in amorphous silica-alumina (B), the acid site is represented by a silanol with a weak acid-base interaction between OH group and Al atom.


Zeolite Amorphous Silica - Alumina

Figure 3: Zeolite vs Amorphous Silica-Alumina [8]

There is a relationship between the protonic acid strength and the angle of TOT bonds (T = Si or Al). The higher the angle, the strongest the acid sites [8]:

**H-MOR (143° - 180°) > H-MFI (133° - 177°) > H-FAU (138° - 147°)**

## 2.3 Benzene Alkylation Catalysts

In addition to zeolites, there are increasing research efforts to develop catalysts for benzene alkylation including pillared clay [9], heteropoly acids [10-11] and super acid [12]. The use of solid superacids with controlled porosity appeared to be a better way of producing 2-phenyldodecane. Yadav et al. [12] reported a superacidic zirconia-based mesoporous catalyst with high activity, selectivity, and stability for the alkylation of benzene using 1-dodecene. The effects of various parameters on the reaction rate were studied. The optimum conditions were 1-dodecene: benzene mole ratio of 1:10, catalyst loading of $2 \times 10^{-2}$ g/cm$^3$ at 140 °C. Hu et al. [13] immobilized $AlCl_3$ on MCM-41 mesoporous silica of different pore sizes to form a novel shape-selective catalyst for

benzene alkylation with alpha olefins. The selectivity toward the monoalkylated product was strongly influenced by the pore size of the carrier material. This demonstrated the opportunities offered by the micelle-templating method to tailor shape-selective catalysts for reactions with bigger molecules.

Wang et al. [14] reported that the activity of $SO_4^{2-}/ZrO_2$ for benzene alkylation was in proportion to the content and the strength of medium acid site. However, the distinct deactivation of catalyst was also observed in the alkylation, the accumulation of hydrocarbon fragment and their removal were mainly reasons of $SO_4^{2-}/ZrO_2$ deactivation. The disadvantage of the solid catalysts is that they are easily deactivated because of the accumulation of heavy products in the channels and reactive sites in the catalysts. Most solid catalysts suffer a poor product selectivity in the range of 26~33% and even worse a serious deactivation problem.

Some other approaches involve the use of ionic liquids [16,12]. Ionic liquids are primarily mixtures of low melting salts such as imidazolium halides, pyridinium halides, or phosphonium halides. The active catalyst for alkylation of benzene by olefins is formed by addition of $AlCl_3$ or other such Lewis acid. DeCastro et al. [15] found that catalysts were active for benzene alkylation with selectivity reaching 98% to monoalkylated products at 99% conversion of dodecene at 80°C. However, the disadvantages of this approach include the difficulty in regeneration of the ionic liquid after extended time on stream and the instability of many of these systems in the presence of water.

The following sub-sections present a review of papers on the alkylation of benzene using zeolite-based catalysts such as Y, beta, mordenite and others.

### 2.3.1 Zeolite based catalysts

Zeolites are widely used as microporous acid catalysts in oil refining and petrochemical synthesis. They have been shown as one of the most promising alkylation catalysts and their use in LAB synthesis has been attempted for some time. Venuto et al. [16] pioneered the zeolite catalyst research for LAB synthesis early in 1970s. However, because of short cycle length, zeolite catalysis has not been industrialized yet. Only very few catalytic stability data has been reported at industrial conditions. Sivasanker and Thangaraj [17] indicated that in terms of selectivity in 2-phenylalkane, HF and RE-Y zeolite were the lowest catalysts in the range of only 14~20%, mordenite was the most outstanding one with a selectivity up to 64%.

Although zeolite catalysts have not been used in industrial detergent alkylation processes, there are a good number of reviews in the literature describing their use in detergent alkylation [18]. It is generally shown that large-pore zeolites with three-dimensional topology are effective in producing LAB with a reasonably high turnover frequency. Smaller 12-member rings (MR) pore size zeolites with three dimensional topology, such as BEA and one dimensional topology, such as MTW, and 10-MR zeolite such as MFI are not effective in providing stable production of LAB. One dimensional 12-MR zeolites, such as mordenite appeared to be effective in carrying out the alkylation reaction, and are more selective towards 2-phenylalkane in the alkylation products.

Mériaudeau et al. [19] compared the performance of various zeolites using a batch reactor at 100-200°C for the alkylation of benzene with 1-dodecene. The results indicated that dealuminated HY zeolites were apparently the most suitable catalysts. H-ZSM-5, H-ZSM-12 showed almost no activity for the production of LAB, due to the small size of the channels. The reaction was influenced considerably by diffusion.

Tian et al. [20] evaluated a series of MCM-22 zeolite catalysts modified with phosphorus in the alkylation of benzene with 1-dodecene using a fixed-bed reactor. The results showed that the crystal structure was intact after modification, but there was partial breaking of the Al–O–Si bonds, and some tetrahedral aluminum was converted to hexahedral aluminum. A proper phosphorus content can improve the selectivity to 2-dodecylbenzene and the catalytic stability of the MCM-22 catalyst for the alkylation of benzene with 1-dodecene. The maximum yield of 2-dodecylbenzene was obtained with a phosphorous content of 0.5%.

Jan and Riley [18] disclosed a process wherein a layered zeolite-based catalyst was used for the alkylation of benzene with a substantially linear olefin. The layered catalyst allowed for shifting the operating conditions to increase the alkylation of benzene, while reducing the amount of isomerization of the alkyl group. This is important for increasing the quality of the alkylbenzene by increasing the linearity of the alkylbenzene. Zeolites that can be used in this invention include UZM-8, Faujasite, beta, MTW, MOR, LTL, MWW, EMT, UZM-4 and mixtures thereof.

#### 2.3.1.1 Y-Zeolite based Catalysts

One of the most important zeolites applied in catalysis is zeolite Y, which is used in processes such as fluid catalytic cracking (FCC), hydrocracking, and alkylation in oil refining and petrochemical synthesis. Y-zeolite based catalysts seem to be one of the most suitable alternative catalysts for LAB synthesis. Due to the particular dimensions of its channels and cavities, Y-zeolite offers a good compromise between easy access to its catalytic active sites and restricted formation of bulky branched molecules. In this way, Y zeolite shows a good alkylation activity with high selectivity to LAB. As the catalyst

Si/Al ratio increases, the concentration of the acid sites diminishes while the acid strength of the remaining sites increases. Therefore, by dealumination one could fine tune the acid properties of the zeolite in order to achieve a catalyst with optimal acid properties for the desired application [21].

Yuan et al. [22] investigated catalytic activity, stability and selectivity of USY zeolite catalyst for alkylation of benzene with 1-dodecene using a continuous fixed bed high pressure microreactor. It was found that the catalytic activity and stability depend closely on the pretreatment temperature of catalyst and reaction conditions. The best result was obtained at 120 °C and 3.0MPa with 8 molar ratio of benzene to 1-dodecene, and 4 $h^{-1}$ weight hourly space velocity (WHSV) of reactant over the catalyst with the pretreatment temperature of 500 °C. Under this condition, the reaction conversion was nearly 100% and no deactivation was observed within the employed 50hr of time-on-stream with the selectivity of 2-phenyldodecane being 22%.

Cao et al. [23] found that the selectivity to the most desired 2-phenyl dodecane isomer was found to increase with increased porous constraints. Yields in the preferred isomer over beta catalysts were very close to those provided by the Y-zeolite open structure catalysts in spite of a much lower conversion over beta catalysts. Deactivation affected not only the alkylation reaction, but the isomerization of the olefin as well, over beta catalysts. The formation of the bulkiest LAB isomer within the channels of the beta catalysts probably resulted in a rapid clogging of the pores thus limiting the conversion to quite low values.

Carciun et al. [24] used three USY zeolites with bulk Si/Al ratios of 6, 13 and 30 for the alkylation of benzene with 1-octene at temperatures ranging from 70 to 100°C,

benzene/1-octene feed molar ratios ranging from 1 to 10 and 1-octene conversions between 10% and 99%. Octene isomers were formed consecutively from double bond isomerization of 1-octene; 2-, 3- and 4-phenyloctanes were obtained as alkylated products. Catalyst deactivation was less important at 1-octene conversions higher than 90%. The catalytic activity increased with increasing Si/Al ratio while the selectivities were not affected. The higher rates observed for the catalyst with the higher average acid strength was traced back to a decrease in the activation energy for the protonation step leading to an increased concentration of carbenium ions on the catalyst surface that compensated for the higher activation energies for the deprotonation and alkylation steps. The constant selectivities were explained by a similar dependency of the different elementary steps on the acid site strength. Riley et al. [25] disclosed a method and process for the the alkylation of benzene using a small crystal Y-zeolite at a benzene to olefin molar ratio of 30:1, inlet temperature of 90° C., and 3.79 $hr^{-1}$ LHSV. The invention also relates to a mixture of Y-zeolite with at least one other zeolite from ZSM-4, ZSM-12, ZSM-20, ZSM-38, MCM-22, MCM-36, MCM-49, beta, and mordenite.

#### 2.3.1.2 Beta-based Catalysts

Han et al. [26] reported that deactivation of zeolite H-Beta became worse by using real feed with cycle life less than 20 h. They showed that oligomers of olefinic feed compounds caused catalyst deactivation. Feed impurities such as C4–C7 alkylbenzenes, bulky aromatics and water can deactivate zeolite H-beta. According to some literatures, the deactivated catalyst contained more 5-isomer LAB and 6-isomer LAB. Therefore, introducing mesopores in zeolite can improve zeolite stability by enhancing the diffusivity of products.

Hornacek et al. [27] performed alkylation of benzene with 1-alkenes ($C_6$–$C_{18}$) in liquid phase at 160–200 °C over beta zeolites with Si/A molar ratio 12.5–75.0. With increasing alkyl chain length, the conversion of 1-alkene decreased. The alkylation activity decreased with increasing Si/Al ratio of Beta-zeolite due to the enhancement of the portion of Lewis acid sites in total acidity, resulting in greater dimerization/oligomerization activity and consequently in more rapid deactivation of beta-zeolites.

Bordoloi et al. [28] studied a composite catalyst of AlMCM-41/Beta zeolite for benzene alkylation with 1-decene, 1-octene and 1-dodecene. The effect of temperature, reactant molar ratios and catalyst weight on 1-dodecene conversion and products selectivity were studied. The composite catalyst was found to be the highly selective towards the formation 2-dodecylbenzene. Under the reaction conditions of 120 °C, benzene/1-dodecene molar ratio 10 and time 2 h, the catalyst gave 48% dodecene conversion with 76%, 2-dodecylbenzene selectivity. Significant improvement in catalytic activity has been achieved by composite catalyst as compared to Al-MCM-41. Although zeolite Beta and composite catalyst gave similar conversion of dodecene, the composite catalyst showed higher selectivity towards 2-dodecylbenzene, which could be due to higher diffusibility of 2-dodecylbenzene isomer in the composite material.

#### 2.3.1.3 Mordenite-based Catalysts

Knifton et al. [29] demonstrated that LAB comprising >80% 2-phenyl isomer content can be prepared in sustainable high yields from detergent-range linear α-olefins via regioselective benzene alkylation using reactive distillation technology in

combination with HF-treated mordenite catalysis. It was claimed that the acid-modified mordenite catalysts provided enhanced shape-selective alkylation performance.

There are three types of mesoporous zeolite materials, namely hierarchical zeolite crystals, nanosized zeolite crystals, and supported zeolite crystals [30]. The hierarchical zeolites possess crystallographic micropores of the given zeolite structure, additional intracrystalline mesopore system and intercrystalline pore system as a consequence of the packing of the zeolite crystals. The intracrystalline mesopore could be generated by template method. On the other hand, the nanosized zeolite crystals with typical crystal sizes below 100 nm possess typical crystallographic micropores and intercrystalline pores. The mesopore size and shape could be manipulated by controlling the size, shape, and packing of the nanosized zeolite crystals. The supported zeolite is a composite material, which can be prepared from zeolite and support mixtures, or directly synthesized as monolith structure. The pore sizes of the mesopores are largely determined by support. The mesopores are versatile from adjusting zeolite/support formulation.

Mériaudeau et al. [19] concluded that while H-mordenite also showed very low catalytic activity, dealuminated H-mordenite exhibited a significant activity and a very high selectivity for the production of 2-phenyldodecane which is the less bulky among the other phenyldodecane isomers. The mesoporosity generated within dealuminated mordenite was responsible for these observations. On the other hand, the difference in product selectivity in various zeolite types was always attributed to the differential product diffusivity. Cao et al. [23] suggested that secondary pore of dealuminated mordenite plays a prominent role in selectivity. However, rigorous study on the origin of product selectivity is still lacking.

Wang et al. [14] compared the activities of H-mordenite, H-USY, HY, and H-ZSM-5 in the alkylation of benzene with 1-dodecene in a batch reactor at 140°C and 10 atm. H-mordenite showed the highest selectivity of 78.2% for 2-phenyldodecane with 100% conversion. Depending on the catalyst amount (from 0.5 to 1.0 g) and the molar ratio of benzene to 1-dodecene (from 7 to 10), the conversion of 1-dodecene varied in the range from 63.8 to 100%. Furthermore, modification of H-mordenite by dealumination using nitric acid and by solid ion exchange with $Mg^{2+}$ and $Fe^{3+}$ ions led to the improvement of the selectivity for 2-phenyldodecane, and simultaneously reduction of the conversion of 1-dodecene was observed.

In other studies, Tsai and co-workers [31] reported that steam post treatment can stabilize and enhance mordenite activity showing cycle length longer than 600 hrs and high product selectivity of 2-phenylalkane at 67%. Furthermore, zeolite activity can be more stable at elevated reaction temperatures. Boveri et al. [32] found that mordenite-based catalysts obtained by combined steam dealumination and acid washing show a dramatic increase in the intrinsic activity and a significantly lower tendency to suffer deactivation when compared to the parent zeolite and samples obtained by acid treatments.

Li et al. [33] studied three methods for preparing mesoporous mordenite using the following:

i. Acid leaching followed by base leaching of a conventional mordenite

ii. Amphiphilic organosilane and

iii. Carbon as secondary template.

The acid leaching method yielded a real mesoporous mordenite exhibiting much higher catalytic activity than conventional mordenite in the alkylation of benzene.

Ponomareva et al. [34] investigated catalysts having a combined micro-mesoporous structure with different amounts of mesopores obtained by the hydrothermal recrystallization of mordenite and beta zeolites. The formation of transport pores and an increase in the accessibility of acid sites as a result of recrystallization under mild conditions facilitated an increase in the activity, with a high selectivity for linear phenyldodecanes being retained. The mordenite-based catalysts were more active than beta-zeolite tested separately.

## 2.4 Reaction Conditions and Pathway

The reaction conditions used in benzene alkyltion were selected to minimize isomerization of the alkyl group and minimize polyalkylation of the benzene, while trying to maximize the consumption of the olefins to maximize product [35]. Laboratory reactors were either batch or continuous flow fixed-bed reactors. Alkylation conditions included a reaction temperature between 80° C. to 175° C. The pressures in the reactor were ranged from 2 MPa to 3.5 Mpa. To minimize polyalkylation of the benzene, the aryl to monoolefin molar ratio was between 5:1 to 35:1. The average residence time in the reactor helps control product quality, and the process is operated at a liquid hourly space velocity (LHSV) from 0.3 to 6 $h^{-1}$. The isomerization of the alkyl group is one of the main problems during LAB production and therefore reducing the quality of the product. Understanding the reactions, catalysts used, and controlling the reaction environment associated with the production of LAB can produce a higher quality product with lower loss of raw materials. A reaction network was developed based on the chemistry of the

process and the observed product distribution [35, 36]. Olefins may undergo consecutive isomerisation and can react with benzene and produce phenylalkanes. Several mechanisms have been suggested in the literature for this type of reactions. The most successful ones involve the formation of carbenium and/or carbonium ions as intermediates, although the detailed nature of the intermediates is the subject of ongoing investigations.

Tsai et al. [37] proposed a reaction pathway in Figure 4 to account for the high selectivity of 2-phenyl substituted isomer over mordenite catalyst. As skeleton isomerization of 1-dodecene, equation (1) in Fig. 4, does not proceed over mordenite, 1-dodecene proceeds fast double bond migration, equation (2), forming 2- and 3-dodecyl carbenium ions to alkylate benzene into corresponding LAB isomers. This shape selectivity does not only control LAB isomer selectivity, it also affects coke formation. Two coking schemes are shown in Fig. 4, an alkylation route: equations (3) + (6) and a transalkylation route: equations (7) + (8). By taking the alkylation route, the coke constituents are mono-alkyl benzene and dimmers of olefins; whereas by taking the transalkylation route, the coke is polyalkylbenzene in nature.

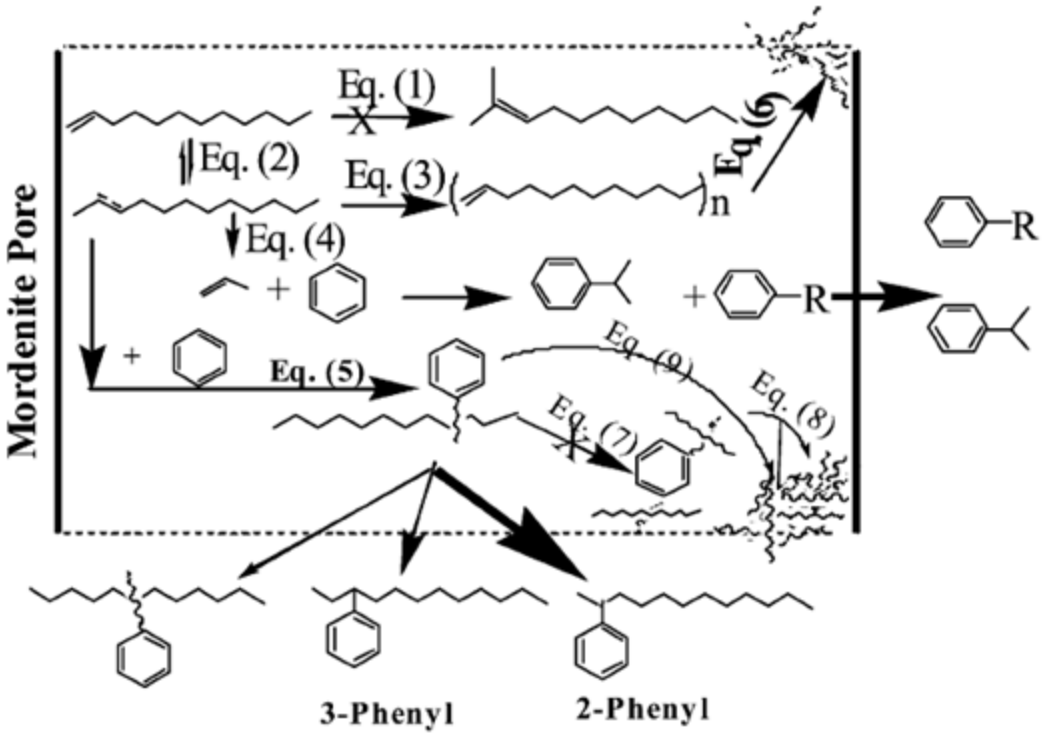



Figure 4: LAB isomers formation in the alkylation of Benzene with dodecene [37]

The formation of primary products that is 2-olefins and 2-phenylalkanes, is observed at low olefin conversions and the rate of double bond isomerization is faster than alkylation. The interpretation of the kinetic results and reactivity patterns resides in:

i. Acid strength controlling the activation energy of the protonation step and consequently concentration of surface carbenium ions and

ii. The barriers to the products diffusion from the microporous interior through pore mouths of various sizes and shapes.

It is interesting to note that most studies have been conducted under reaction conditions where poly-alkylated benzene was produced in lower concentrations. Guisnet and coworkers showed that transalkylation appears to be another pathway to produce mono-

alkylated benzene in toluene alkylation with 1-heptene using a relatively low molar ratio of toluene to olefin at 90 °C [38].

## 2.5 Major Findings of Literature Review

The literature review revealed the following findings:

- Conventional production of LAB is practiced using HF acid or solid acid catalysts. HF is corrosive and causes environmental pollution while current solid acid catalysts suffer rapid deactivation (solved by regeneration by washing with benzene).

- There is one LAB production plant in Jubail, Saudi Arabia using Detal solid acid catalyst (70,000 tons/yr) and another plant is in planning stage in Yanbu.

- A wide range of solid catalysts with considerable acidity have been tried for the alkylation of benzene with long chain olefins into LAB. These catalysts include heteropoly acids, sulphated zirconia, acidic clays, and acidic zeolites.

- The performance of the LAB process is characterized to a significant extent by the activity and selectivity of the alkylating catalyst in the operating environment of the process.

- Because of the ongoing fundamental studies on reaction mechanism and catalyst properties, significant progress is being made to improve the selectivity, catalytic stability, and long-term stability of these solid acids under industrial operating conditions.

- The use of catalysts based on high- acid and good thermal stability zeolites opens entirely new opportunities for the selective formation of the desired alkylation products due to the specific characteristics of these zeolites.

- Utilizing large-pore zeolites represents one of the challenging routes and would be a significant step forward for LAB production. Introducing mesopores can improve zeolite stability by enhancing the diffusivity of products. Nevertheless, there is no systematic study on the stabilization effect of mesopore structures.

- Methods to enhance molecular transport involve synthesis of zeolites with larger micropores (1–2 nm), synthesis of nanosized zeolites (short micropores), as well as the creation of mesopores (2–50 nm) in zeolite crystals using acid or base leaching, carbon templating, or mesopore structure-directing agents.

- Potential catalysts for further investigation include mesoporous mordenite and beta zeolites.

## 2.6 Commercial catalysts for linear alkylbenzene synthesis

Both HF and $AlCl_3$ being homogeneous acid catalysts lead to formation of all five isomers from 2- to 6-phenyldodecanes but with varying distribution. In addition to being environmentally safe, the heterogeneous catalyst is advantageous for enabling the use of ordinary materials of construction, easy separation of product, and elimination of HF waste byproduct. But for a successful process, the solid acid catalyst should be active, selective, regeneration-friendly, and stable over prolonged periods of operation to be economical compared to liquid hydrofluoric acid. In developing a solid catalyst, controlling the formation of carbonaceous deposit is critical to making a regenerate-able

and stable catalyst. Many solid acids, including clays, pillared clays, zeolites, metal oxides and sulfides, sulfated zirconia, heteropoly acids (HPAs), and immobilized ionic liquids, have been found to be active for the alkylation of benzene with various olefins. Zeolites have been widely evaluated for the production of linear alkylbenzenes. The selectivity of these materials is always skewed to the 2-phenyldodecane because of the size restrictions of the zeolite pores. [1]. Table 4 depicts the distribution of LAB isomers using different catalysts for alkylation of Benzene with 1-dodecene at 135 °C, 7 bar, WHSV 0.8 $h^{-1}$, benzene: dodecene (mole) ratio = 10.

Table 4: LAB isomer distribution for different catalysts [36]

| **Catalyst** | **2-PD** [a] | **3-PD** | **4-PD** | **5-PD** | **6-PD** |
|---|---|---|---|---|---|
| $SiO_2$-$Al_2O_3$ | 33.4 | 21.9 | 14.8 | 15.6 | 14.2 |
| H-Y | 29.5 | 20.2 | 17.1 | 16.9 | 16.3 |
| RE-Y | 17.6 | 19.1 | 19.8 | 22 | 21.5 |
| H-Beta | 39.1 | 26.4 | 18.9 | 10.8 | 4.8 |
| H-Mordenite | 63.7 | 35.4 | 0.9 | - | - |
| HF [b] | 20 | 17 | 16 | 23 | 24 |
| $AlCl_3$ [c] | 32 | 22 | 16 | 15 | 15 |

a- PD = Phenyldodecane.

b- Data of Alul: Temperature = 328 K

c- Data of Olson: Temperature = 326 K

## 2.7 Summary of research efforts

### 2.7.1 Zeolites

Table 5: Catalytic performance of zeolites for Benzene alkylation reaction [3]

| Zeolite | | | | | |
|---|---|---|---|---|---|
| **Catalyst** | **Temperature ($^0$C)** | **$C_{12}H_{24}$ Conversion** | **Benzene/Olefin** | **Linearity** | **Life (hr)** |
| Y | 155 | 99% | 15:1 | 91.7% | 140 |
| Beta | 155 | 99.5% | 15:1 | 78.5% | 120 |
| ERB 1 | 155 | 98.7% | 15:1 | 88.45% | <40 |
| L | 155 | 92.8% | 15:1 | 72.92% | <20 |
| CaY | 155 | 99.8% | 15:1 | 41.8% | >160 |
| ReY | 155 | 99.8% | 15:1 | 91.61% | 120 |
| LaY | 155 | 99.8% | 15:1 | 94.89% | 160 |

### 2.7.2 Pillared clay

Table 6: Pillared Clays for alkylation reaction [3]

| Pillared Clay | | | | | |
|---|---|---|---|---|---|
| **Catalyst** | **Temperature ($^0$C)** | **$C_{12}H_{24}$ Conversion** | **Benzene/Olefin** | **Linearity** | **Life (hr)** |
| Al-PILC | 155 | 93.1% | 15:1 | 98.5% | 16 |
| AlCe-PILC | 155 | 100% | 15:1 | 93.8% | 140 |
| AlGaCeMg-PILC | 155 | 100% | 15:1 | 94.2% | 240 |

### 2.7.3 Clay supported heteropolyacids:

Table 7: Clay supported heteropolyacids as catalyst for Benzene alkylation reaction [3]

| **Clay supported heteropolyacids** | | | | |
|---|---|---|---|---|
| **Catalyst** | **Temperature ($^0$C)** | **$C_{12}H_{24}$ Conversion** | **Benzene/Olefin** | **Linearity** |
| DTP/K-10 | 150 | 97% | 10:1 | 94% |
| DMP/K-10 | 150 | 92% | 10:1 | 80% |
| DTS/K-10 | 150 | 91% | 10:1 | 79% |
| DTP/Silica | 150 | 57% | 10:1 | 77% |
| DTP/carbon | 150 | 0% | 10:1 | 0% |
| $AlCl_3$/$FeCl_3$/K-10 | 150 | 32% | 10:1 | 65% |
| Al-exchanged K-10 | 150 | 22% | 10:1 | 75% |
| Cr-exchanged K-10 | 150 | 12% | 10:1 | 71% |
| Sulphated Zirconia | 150 | 12% | 10:1 | 62% |
| Zr-exchanged K-10 | 150 | 10% | 10:1 | 65% |
| Filtrol-24 | 150 | 85% | 10:1 | 69% |
| K-10 | 150 | 71% | 10:1 | 57% |

## 2.8 Criterion for a catalyst to be commercially acceptable

Linearity = 90%

Selectivity = 85%

Conversion = 98%

and a reasonable period of time for which catalyst maintains these characteristics [35].

where,

Linearity = (Moles of Linear Monoalkyl benzene produced/Moles of Monoalkyl produced) × 100

Conversion = (Moles of Dodecene consumed/Moles of Dodecene initially present) ×100

(The conversion is always reported in terms of Olefin (dodcene), because Benzene is taken in excess)

Selectivity = (Moles of Monoalkyl Benzene produced/Moles of Dodecene consumed) ×100.

## 2.9 Problem statement and scope of this work

Since the commercially available catalysts Hydrofluoric acid (HF) and Friedel-Craft catalyst ($AlCl_3$) are difficult to handle corrosive and cause environmental pollution and also the homogeneous catalysis cause product separation difficulties. Moreover, from table 4, it is evident that zeolite based catalysts e.g., mordenites are more selective towards 2-Phenyldodecane (63%), which is the most rapidly biodegradable isomer of LAB, as compared to HF (20%) so there is a tremendous scope to investigate inherent solid acids e.g., zeolites for alkylation reaction.

# CHAPTER 3

# RESEARCH OBJECTIVES

## 3.1 General objective

The major objective for this research effort is to replace corrosive Hydroflouric acid (homogeneous catalyst) with environment an friendly zeolite based catalyst (Heterogeneous catalyst) for Benzene alkylation.

## 3.2 Specific objectives

The present research was done to achieve the following goals:

I. Studying the alkylation reaction (Benzene with dodecene) over zeolite based catalysts
    1) Examine the effects of zeolite topology (i.e., USY, Mordenite, Beta)
    2) Effects of $SiO_2/Al_2O_3$ ratio.
    3) Effects of post modification of zeolites by alkaline treatment.

II. Detailed characterization of catalysts under investigation.

III. Catalytic performance evaluation for alkylation reaction of benzene with dodecene in a fixed bed reactor.

IV. Identification of the elementary steps in the alkylation reaction and develop a kinetic model based on the suggested mechanism.

# CHAPTER 4

# EXPERIMENTAL SECTION

This section covers the details of materials used for the study and the experimental techniques used for their characterization.

## 4.1 Materials

No modification was carried out on all materials utilized in this experiment i.e., they were used the same way they were bought. The main reagents used were 0.2M NaOH solution, 0.1N $NH_4Cl$ solution and Pyridine (for Bronsted and Lewis acid sites measurements).

## 4.2 Zeolite post-synthesis treatment

### 4.2.1 Desilication procedure:

The parent beta and mordenite zeolites were subjected to alkaline treatment to introduce mesoporousity in zeolite structure. Desilicated mordenite (DMOR-18, DMOR-40) were prepared by treating the parent zeolites with a NaOH solution of 0.2 M at 60 °C for 0.5 h. The solid was then further ion exchanged with a 0.1 M $NH_4Cl$ solution at 60 °C for 4 h. The desilicated beta (DBEA-24 & DBEA-40) were prepared by slurrying the zeolite sample (5 g) in 350 ml of 0.05 M NaOH solution at 60 °C for 1 h. The zeolite/alkali slurry was immediately quenched in ice bath to stop further reaction, filtered, dried and ion exchanged. All the ion-exchanged zeolites were calcined at 650 °C for 3 h at a heating rate of 3 °C/min.

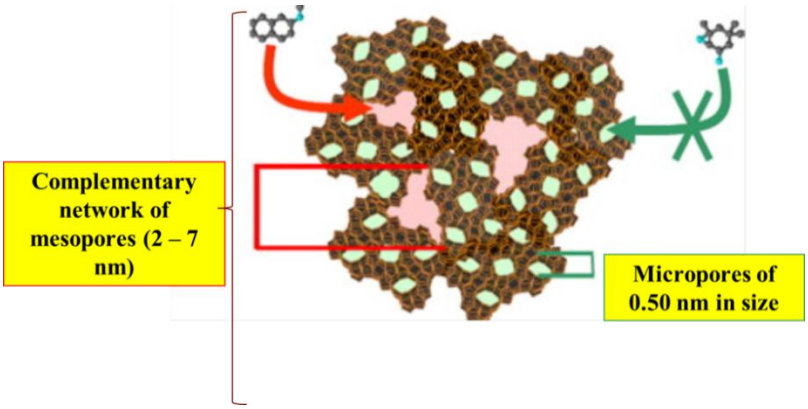



Figure 5: Alkaline treatment (desilication) [59]

## 4.3 Characterization of catalyst

The acidic properties of the zeolites were measured using a Nicolet 6700 FTIR spectrophotometer (Thermo Scientific) equipped with a high temperature vacuum chamber using pyridine as a probe. The zeolite sample (50 mg) was pressed and placed in a sample holder for pretreatment at 550 °C under vacuum for 1 h. The sample was then cooled to 100 °C and the spectrum was recorded. The physically adsorbed pyridine was removed by heating the sample at 150 °C, 250 °C and 400 °C under vacuum ($10^{-5}$ mbar) for 40 min. The removed material was cooled to room temperature and then the spectrum was recorded again. The acidity was calculated using the extinction coefficient (0.75) of the bands of pyridine adsorbed at Brønsted and Lewis acid sites.

The surface area of the catalysts was measured using a Quantachrome Autosorb 1-C analyzer nitrogen adsorption-desorption measurements at -196 °C according to ASTM D3663 standard method. Prior to nitrogen adsorption, the catalyst was evacuated for 2 h at 350 ºC. Micropore volume, $V_{micro}$, and total pore volume, $V_{tot}$, were determined using

t-plot method. The mesopore volume, $V_{meso}$ was estimated by subtracting micropore volume, $V_{micro}$, from total pore volume, $V_{tot}$.

The elemental analysis for Si and Al was measured using ICP Optical Emission Spectrometer, Ultima 2, Horiba Scientific. 50 mg catalyst sample was fused with 300 mg of Lithium metaborate in a muffle furnace at 950 °C for 15 minutes. The fused product was dissolved in 20 ml of 4 % $HNO_3$. The solution was further diluted with deionized water to make a total volume of 50 ml.

The powder X-ray diffraction (XRD) was recorded on a Rigaku Miniflex II X-ray diffractometer using nickel filtered radiation at 40 kV and 30 mA. Start angle 5, stop angle 60, scan speed 1 and sample width of 0.02.

The total acidic strength of the catalyst was measured using ammonia TPD. Temperature-programmed desorption (TPD) of ammonia was performed in BEL-CAT-A-200, chemisorption apparatus that consists of a gas mixing unit allowing both continuous and pulsed reactant dosing, U-tube quartz micro-reactor with a thermocouple placed inside the sample, and a thermal conductivity detector (TCD). The sample (50mg) was pretreated in a flow of He (50 mL/min) at 500 ºC for 1 h. Then the sample was exposed to He/$NH_3$ mixture (95/5 vol%) or He/$CO_2$ (95/5 vol%) at room temperature for 30 min. TPD was performed in He flow (50 mL/min) at a heating rate of 10 ºC/min, and the desorbed $NH_3$ was monitored by a TCD detector.

## 4.4 Chemicals and Catalysts

Benzene and Dodecene (research grade) were obtained from Sigma Aldrich chemicals. The list of catalyst investigated and their properties are provided in Table 8.

### 4.4.1 Catalysts:

Table 8: Catalysts investigated for alkylation of Benzene with 1-dodecene

| Zeolite Sample | Pore Structure | Sample code | Description* | $SiO_2/Al_2O_3$ ratio |
|---|---|---|---|---|
| Ultra-stable Y | 3D, 7.4 Å | USY | Parent zeolite from Tosoh | 6.5 |
| Beta | 3D, 7.3 x 6.5 and 5.6 x 5.6 Å | BEA-24 | Parent beta from Tosoh | 24 |
| | | DBEA-24 | Desilicated BEA-24, treated with 0.05 M NaOH solution for 1 h at 100 °C | - |
| | | BEA-40 | Parent beta from Tricat | 39 |
| | | DBEA-40 | Desilicated BEA-40, treated with 0.2 M NaOH solution for 0.5 h at 60 °C | - |
| Mordenite | 2D, 7 x 6.5 and 5.7 x 2.6 Å | MOR-18 | Parent mordenite from Tosoh | 18 |
| | | DMOR-18 | Desilicated MOR-18, treated with 0.2M NaOH solution for 0.5 h at 60 °C | - |
| | | MOR-40 | Parent mordenite from J. Heyrovský Institute of Physical Chemistry | 40 |
| | | DMOR-40 | Desilicated MOR-40 treated with 0.2 M NaOH solution for 0.5 h at 60 °C | - |
| | | MOR-180 | Parent mordenite from Tosoh | 180 |
| | | MOR-20 | Parent mordenite from Zeolyst | 20 |

### 4.4.2 Apparatus and reaction procedure

All experiments were conducted using a 5 ml continuous flow reactor, BTRS Junior, provided by Autoclave Engineers, U.S.A. The reactor tube (SS 316 reactor tube, 10mm ID) was cleaned with Acetone solution and then filled with successive layers of glass wool, Alumina balls, glass wool, 1 g catalyst (0.5 –1 mm mesh size) and glass wool. The reactor tube was provided with a Thermowell 2mm OD. The reaction system was provided with an electric furnace and electric heater to maintain the desired temperature inside the reactor. A 6:1M mixture of benzene and dodecene was introduced into the reaction system using a positive displacement pump at a flow rate of 0.08

ml/min. (4 $hr^{-1}$ space velocity). Nitrogen was introduced with the feed, as a carrier gas, at a flow-rate of 50 ml/min. The reaction system was pressurized at 300 psi and gradually heated at a temperature of 140 $^0$C. The feed along with carrier gas (Nitrogen) were introduced form the top of the reactor. The reaction products were passed through a gas liquid separator where, vaporizedproducts were condensed and collected in liquid form.

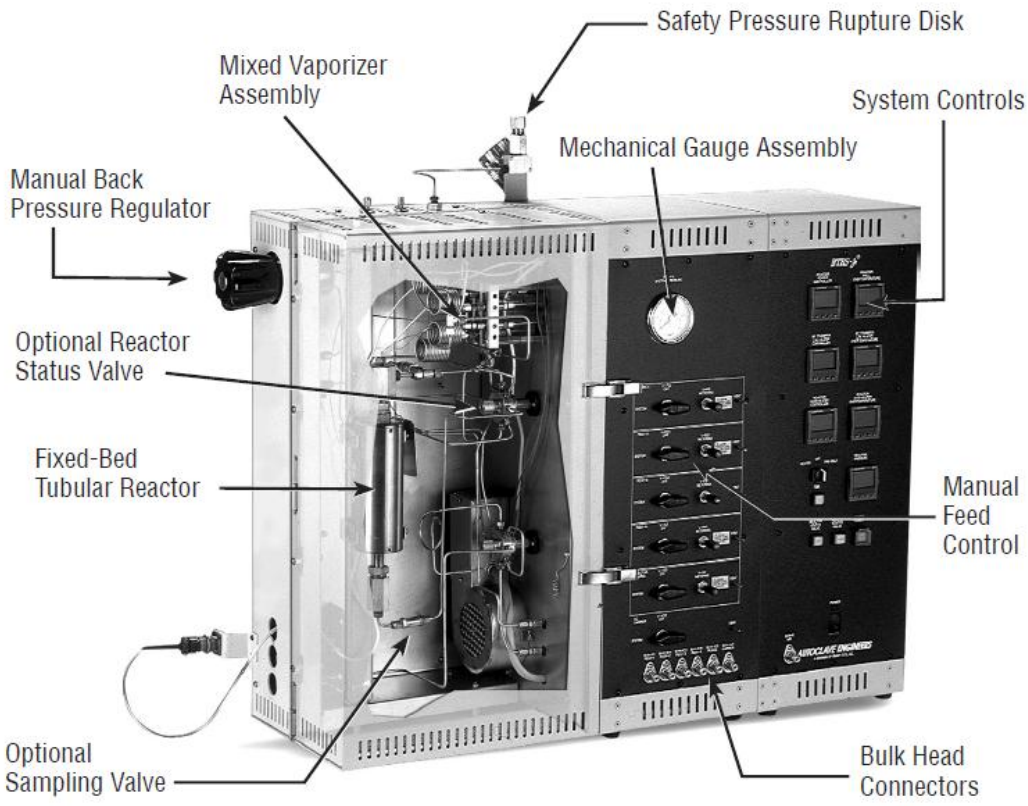



Figure 6: BTRS-Jr. Fixed bed micro reactor [39]

A more detailed schematic diagram of the reaction system is given in the Fig. 7

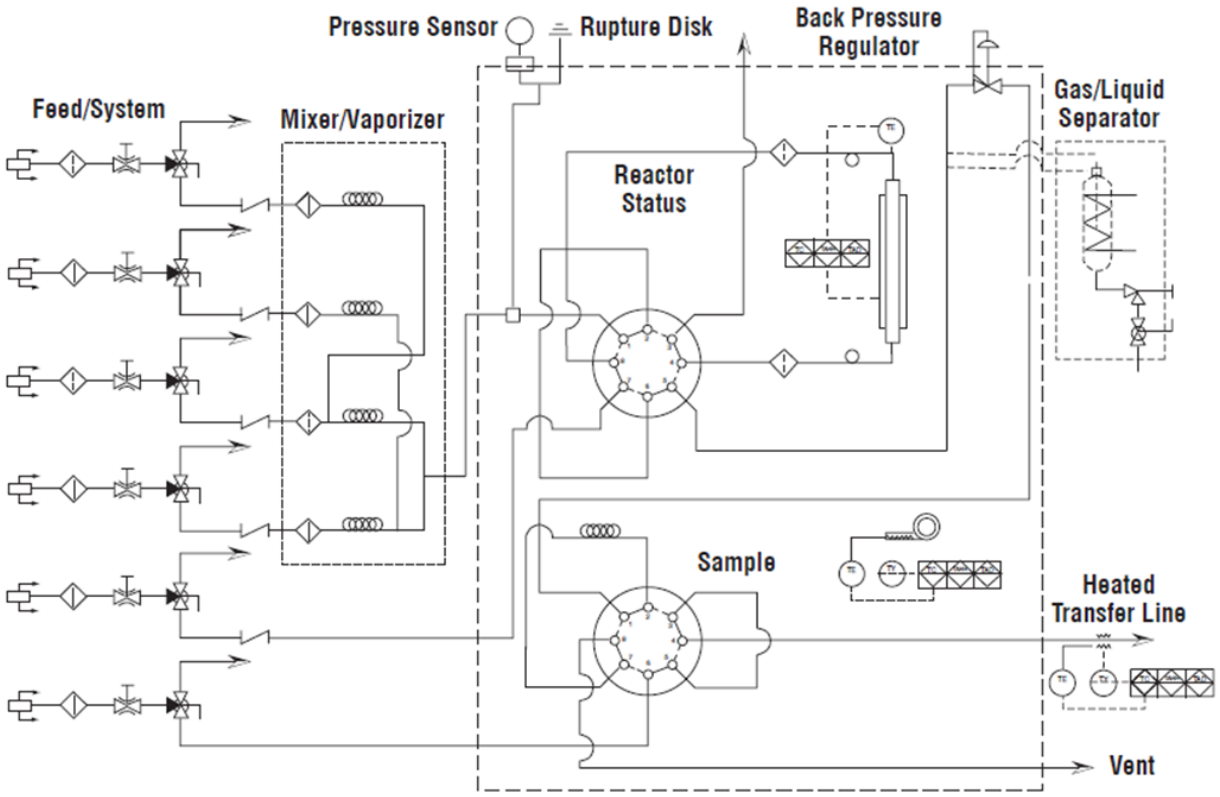



Figure 7: A shcematic diagram of reaction system provided by Autoclave Engineers [39]

### 4.4.3 Product analysis

The product samples were collected at successive time intervals of 1 hour in GC-vials. A Gas Chromatograph (Agilent 7890A), with a flame ionization detector was used to analyze the concentration of product sample. The exact composition of the product sample was determined by using GC-MS (Agilent 5980 C). The product samples were injected manually into the Gas Chromatograph. The weight of feed passed and product collected in one hour was also measured.

The heating rate in the FID for detection of dodecene and LAB isomers were fixed as follows:

- GC column 30 m × 320 µm × 0.25µm
- Initial temperature = 60 $^{o}$C
- Rate 1 = 8 $^{o}$C/min.

  Final temperature = 110 $^{o}$C

  Final heating time = 2 min.
- Rate 2 = 10 $^{o}$C/min.

  Final temperature = 260 $^{o}$C

  Final heating time = 10 min.

Injection temperature = 300 $^{o}$C

## 4.5 Catalytic performance evaluation

The product analysis was carried out using a GC-MS (Agilent 5980) equipped with a FID detector. The GC analysis provides the mass fractions *($X_i$)* of different species. The mass fraction data was further processed to find the concentrations *($C_i$)* of the species using the following equation:

$$\boldsymbol{C_i = \frac{X_i \rho}{M_w}}$$

where, ρ and $M_w$ are the density and the molecular weight of the component *i*, respectively.

### 4.5.1 Conversion:

The catalytic performance of mordenite was evaluated on the basis of 1-dodecene conversion.

$$\boldsymbol{1 - dodecene\ conversion}\ (\%) = \frac{(\boldsymbol{F_{do} - F_d})}{\boldsymbol{F_{do}}} \times \mathbf{100}$$

where, $F_{d0}$ is the molar flow rates of 1-dodecene coming into the reactor, and $F_d$ is molar flow rate of 1-dodecene leaving the reactor. The conversion of benzene was not taken into account given it was used in excess amount.

### 4.5.2 Selectivity of LAB isomers:

$$\textbf{LAB isomer selectivity}\ (\%) = \frac{\mathbf{F_{LAB}}}{\mathbf{F_t}} \times \mathbf{100}$$

where, $F_{LAB}$ is the molar flow rate of all the linear alkylbenzene isomers in the final products and $F_t$ is the total molar flow rate including all dodecene isomers (1- to 6-dodecenes) and LAB isomers (2- to 6-phenyldodecanes).

### 4.5.3 Selectivity of 2-phenyldodecane (2-LAB):

Similarly, the selectivity of 2-phenyldodecane was calculated using the following equation:

$$\mathbf{2-phenyldodecane\ selectivity}\ (\%) = \frac{\mathbf{F_{2-PD}}}{\mathbf{F_t}} \times \mathbf{100}$$

$F_{2\text{-}PD}$ is the molar flow rate of 2-Phenyldodecane in the final products.

# CHAPTER 5

# RESULTS AND DISCUSSIONS

## 5.1 Physical and chemical properties of the catalysts:

The results of ICP chemical analysis ($SiO_2/Al_2O_3$ ratio), surface area and concentrations of acid sites in the parent and desilicated zeolites are presented in the Tables 9 & 10. The XRD patterns of the parent and desilicated MOR (MOR-18, MOR-40, DMOR-18, DMOR-40), BEA (BEA-24, BEA-40 DBEA-24, DBEA-40) are shown in Fig. 8. The framework structure of DMOR-18 and DMOR-40, remained intact after desilication treatment. In the case of DBEA-40 sample, the relative intensity reduced, when compared to parent BEA-40 sample. The crystallinity loss of DBEA-40 was calculated by comparing the most intense d302 peak to that of parent BEA-40. After desilication, a moderate loss in the crystallinity (~32 %) was observed in DBEA-24 sample which was desilicated with 0.05 M NaOH solution.

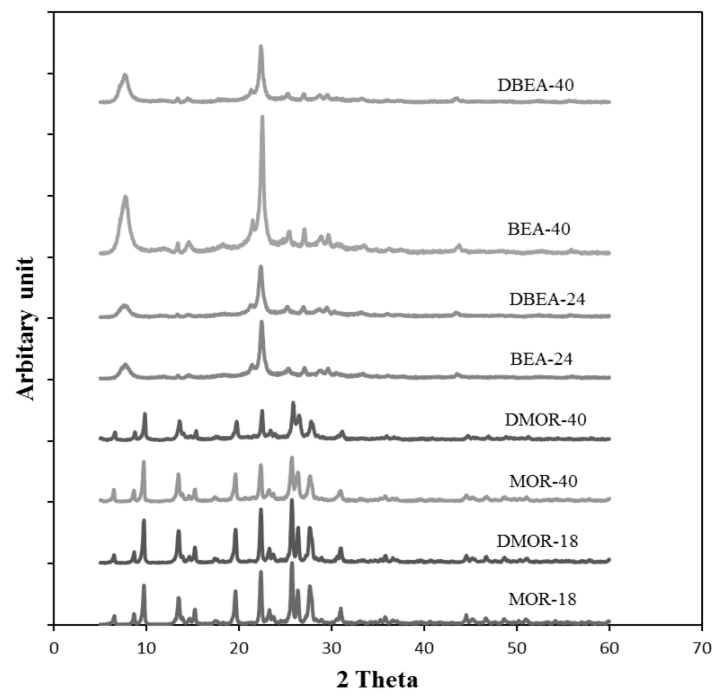



Figure 8: XRD analysis of parent and desilicated MOR-18, MOR-40, BEA-24, BEA-40

Fig. 9 shows the nitrogen adsorption-desorption isotherms for selected zeolite samples. The textural characteristics of all samples are presented in Table 9. The desilicated MOR (DMOR-40) and BEA (DBEA-40) showed a Type IV isotherm with enhanced hysteresis loop compared with parent samples. Desilicated samples exhibited an increase in the BET area accompanied by a significant increase in the mesopore volume (Table 9). This phenomenon can be attributed to the formation for mesopores at the expense of micropores [40]. The BET area and total pore volume results show that FAU zeolite has the highest BET area (533 $m^2/g$) and total pore volume (0.41 $cm^3/g$).

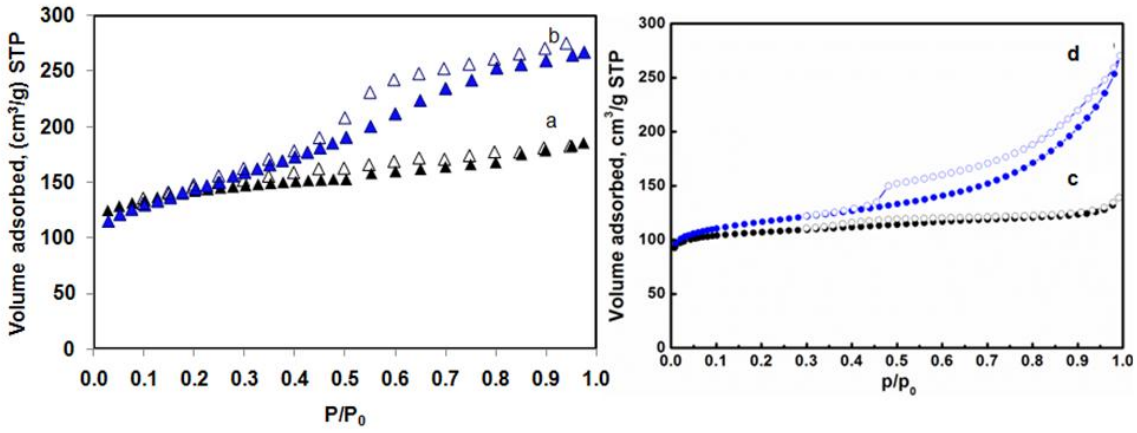



Figure 9: Nitrogen adsorption (•, ▲) and desorption (○, Δ) isotherms of selected parent and desilicated samples: (a) BEA-40 (b) DBEA-40 (c) MOR-40 and (d) DMOR-40

Figure 10, shows the IR absorption bands of hydroxyl stretching vibrations of zeolites under study recorded at room temperature after activation at 400 °C. All parent and desilicated zeolites showed distinctly two characteristic absorption bands around 3740 $cm^{-1}$ and 3610 $cm^{-1}$ due to terminal silanols (Si-OH) and bridging hydroxyl group associated with Brønsted acid sites, respectively [41]. For parent MOR (MOR-18), the peak at 3611 $cm^{-1}$ corresponding to Brønsted acid sites was sharp and highly distinct compared with other zeolites. The impact of desilication is clearly reflected on the desilicated MOR samples (DMOR-18 and DMOR-40), where absorption band of Brønsted acid peak (3615 $cm^{-1}$) is almost disappeared. In addition, for both catalysts, formation of extra-framework aluminum species was observed at 3673 $cm^{-1}$ [42]. In contrast with desilicated DMOR-18, DMOR-40 showed an apparent increase in the intensity of silanol bands indicating the formation of new isolated silanols groups associated with the formation of mesopores [43]. In the case of zeolite BEA, the peak at 3620 $cm^{-1}$ was very weak and broader compared with MOR zeolites. The presence of

such broad peak indicates a wide distribution of acid sites [44]. Apparently, the difference in the intensity of silanol groups after desilication clearly indicates the formation of mesopores.

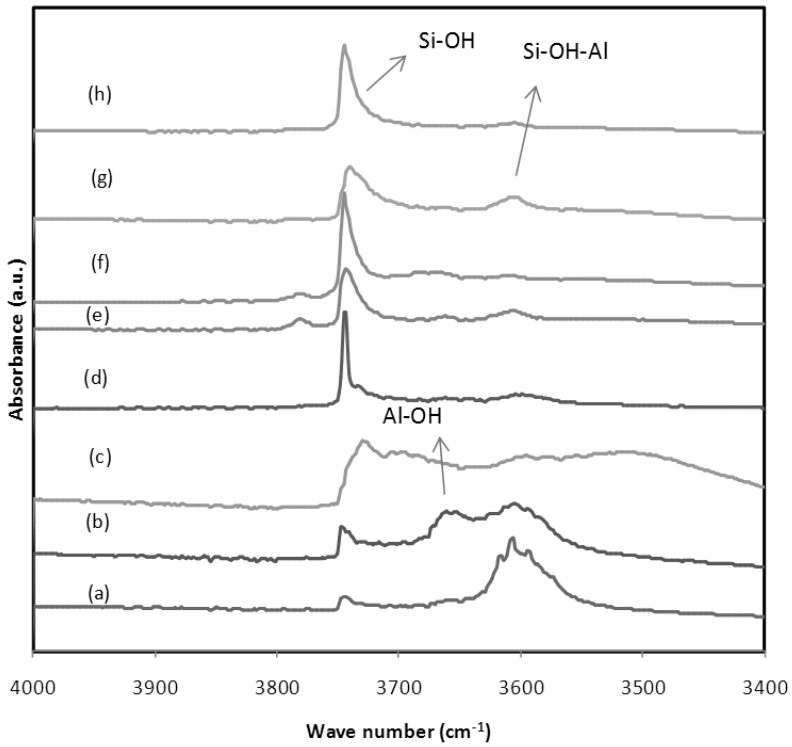



Figure 10: Infra-red spectra of parent and desilicated zeolites : (a) MOR-18, (b) DMOR-18,
(c) MOR-40, (d) DMOR-40, (e) BEA-24, (f) DBEA-24, (g) BEA-40 and (h) DBEA-40

Pyridine FTIR adsorption was used to characterize acidity of all zeolites studied. Fig. 11 shows the FTIR spectra of pyridine adsorbed for parent and desilicated zeolites measured after evacuation at 150 °C. Adsorption of pyridine resulted in the formation of new absorption bands at 1545 (Brønsted) and 1454 (Lewis acid sites) $cm^{-1}$, respectively. The B/L ratios calculated from the IR absorbance intensities are shown in Table 10. Compared to the parent zeolites, the concentration of Lewis acid sites increased whereas the concentration of Brønsted acid sites decreased after alkaline-treatment (Table 10).

Holm et al. reported that upon zeolite treatment with NaOH strong Lewis acid sites are generated, presumably from dislodged framework aluminum [45]. This suggests that more Lewis sites become accessible after desilication, which is further confirmed with the presence of absorption band in the region of Al-OH group around ~3673 $cm^{-1}$ (Fig. 10). Very strong acid sites are not beneficial in the alkylation of benzene with 1-dodecene as oligomerization of olefins can proceed [46]. Thus, acid sites with medium strength are sufficient to catalyze the alkylation reaction.

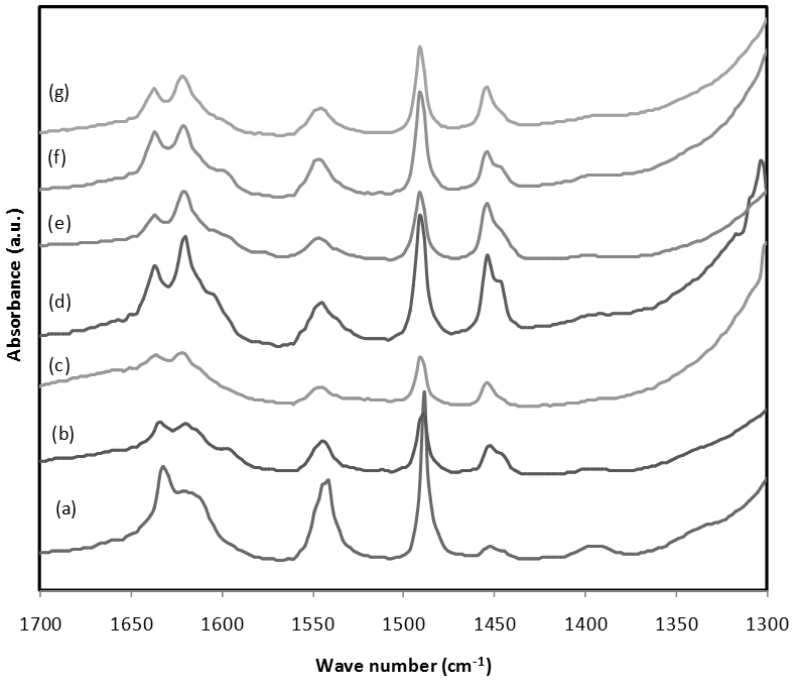



Figure 11: Pyridine-FTIR spectra of parent and desilicated zeolites: (a) MOR-18, (b) DMOR-18, (c) DMOR-40, (d) BEA-24, (e) DBEA-24, (f) BEA-40 and (g) DBEA-40

Table 9: Nitrogen adsorption characteristics

| Zeolite | $N_2$ adsorption characteristics | | | |
|---|---|---|---|---|
| | $S_{BET,}$ ($m^2$/g) | $V_{meso,}$ (cc/g) | $V_{micro}$ (cc/g) | $V_{tot,}$ (cc/g) |
| USY | 533 | 0.21 | 0.20 | 0.41 |
| Beta | | | | |
| BEA-24 | 428 | 0.20 | 0.15 | 0.35 |
| DBEA-24 | 470 | 0.24 | 0.14 | 0.38 |
| BEA-40 | 436 | -- | 0.18 | 0.18 |
| DBEA-40 | 441 | 0.28 | 0.06 | 0.34 |
| Mordenite | | | | |
| MOR-18 | 264 | 0.04 | 0.15 | 0.19 |
| DMOR-18 | 350 | 0.11 | 0.11 | 0.22 |
| MOR-20 | 283 | 0.05 | 0.12 | 0.17 |
| MOR-40 | 302 | 0.07 | 0.14 | 0.21 |
| DMOR-40 | 362 | 0.29 | 0.12 | 0.41 |
| MOR-180 | 514 | 0.05 | 0.24 | 0.29 |

$S_{BET}$: BET specific surface area; $V_{micro}$: micropore volume; $V_{meso}$: mesopore volume; $V_{tot}$: total pore volume

Table 10: Bronsted and Lewis acid sites, total acid strength and elemental analysis of the zeolites under study

| Zeolite | Acidity, pyridine mmol/g | | | Acidity TPD $NH_3$ mmol/g | $SiO_2/Al_2O_3$ ratio |
|---|---|---|---|---|---|
| | B | L | B/L | | |
| USY | - | - | - | 0.33 | 8 |
| **Beta** | | | | | |
| BEA-24 | 0.29 | 0.06 | 4.83 | 0.47 | 29 |
| DBEA-24 | 0.20 | 0.48 | 0.42 | 0.57 | 26 |
| BEA-40 | 0.24 | 0.11 | 2.18 | 0.34 | 38 |
| DBEA-40 | 0.19 | 0.14 | 1.36 | 0.36 | 29 |
| **Mordenite** | | | | | |
| MOR-18 | 0.93 | 0.07 | 13.28 | 0.54 | 19 |
| DMOR-18 | 0.20 | 0.14 | 1.43 | 0.38 | 18 |
| MOR-20 | 1.23 | 0.13 | 9.46 | 0.59 | 20 |
| MOR-40 | 0.26 | 0.13 | 2.00 | 0.21 | 40 |
| DMOR-40 | 0.18 | 0.28 | 0.64 | 0.14 | 36 |
| MOR-180 | 0.05 | 0.22 | 0.23 | 0.04 | 180 |

L: Lewis acidity; B: Brønsted acidity

## 5.2 Catalyst performance evaluation

Based on the findings of literature review different zeolites samples were evaluated for alkylation of benzene with dodecene at 140 °C, 300 psi and at space velocity of 4 $hr^{-1}$.

### 5.2.1 Effect of Zeolite structure

Table 11 presents the catalytic performances of the parent USY, beta (BEA-24 & BEA-40) and mordenite (MOR-18) in terms of 1-dodecene conversion, stability, and selectivity to LAB isomers.

It is evident from Table 11 that USY zeolite exhibited the highest 1-dodecene conversion (97%) and the highest selectivity to LAB isomers (97%) compared with MOR-18 (93%) and BEA-24 (60%). The selectivity to the desired 2-LAB over USY zeolite was 26% and the 2-LAB/3-6 LAB ratio was 0.4 (Table 11). The high selectivity to 3-6 LAB isomers may be attributed to USY large pore opening of 7.4 Å permitting an easy access and diffusion of dodecene into the super-cages of 12.4 Å.

Zeolite BEA-24 exhibited a rapid deactivation; 1-dodecene conversion dropped from 73% to 45% at 6 h of T-O-S (Fig. 12). The selectivity to 2-LAB was less than 24% and the 2-LAB/3-6 LAB isomers ratio was 0.7. The selectivity to dodecene isomers was the highest over BEA-24 (39%) as compared with USY (2%) and MOR-18 (6%). The drop in 1-dodecene conversion with T-O-S for BEA-24 is primarily due to its lower Brønsted acid sites (0.29 mmol/g) compared with MOR-24 (0.93 mm/g) as presented in Table 10. The pore architecture of zeolite beta is a three-dimensional network of channels with diameters of the channel intersections not significantly larger than the diameter of the apertures.

On the other hand, the performance of MOR-18 showed that 1-dodecene conversion and selectivity to LAB isomers were both above 92% (Table 11). The selectivity to 2-LAB (68%) and the 2-LAB/3-5 LAB ratio (2.7) were the highest compared with USY and BEA-24. At longer T-O-S, MOR-18 showed a gradual deactivation, as shown in Fig. 12, which is probably due to the smaller MOR-18 pore diameter compared with BEA-24 and USY (Table 9). During the 6 h T-O-S, the selectivities to total LAB, 2-LAB, and dodecene isomers for the three zeolites were constant regardless of any change in 1-dodecene conversion.

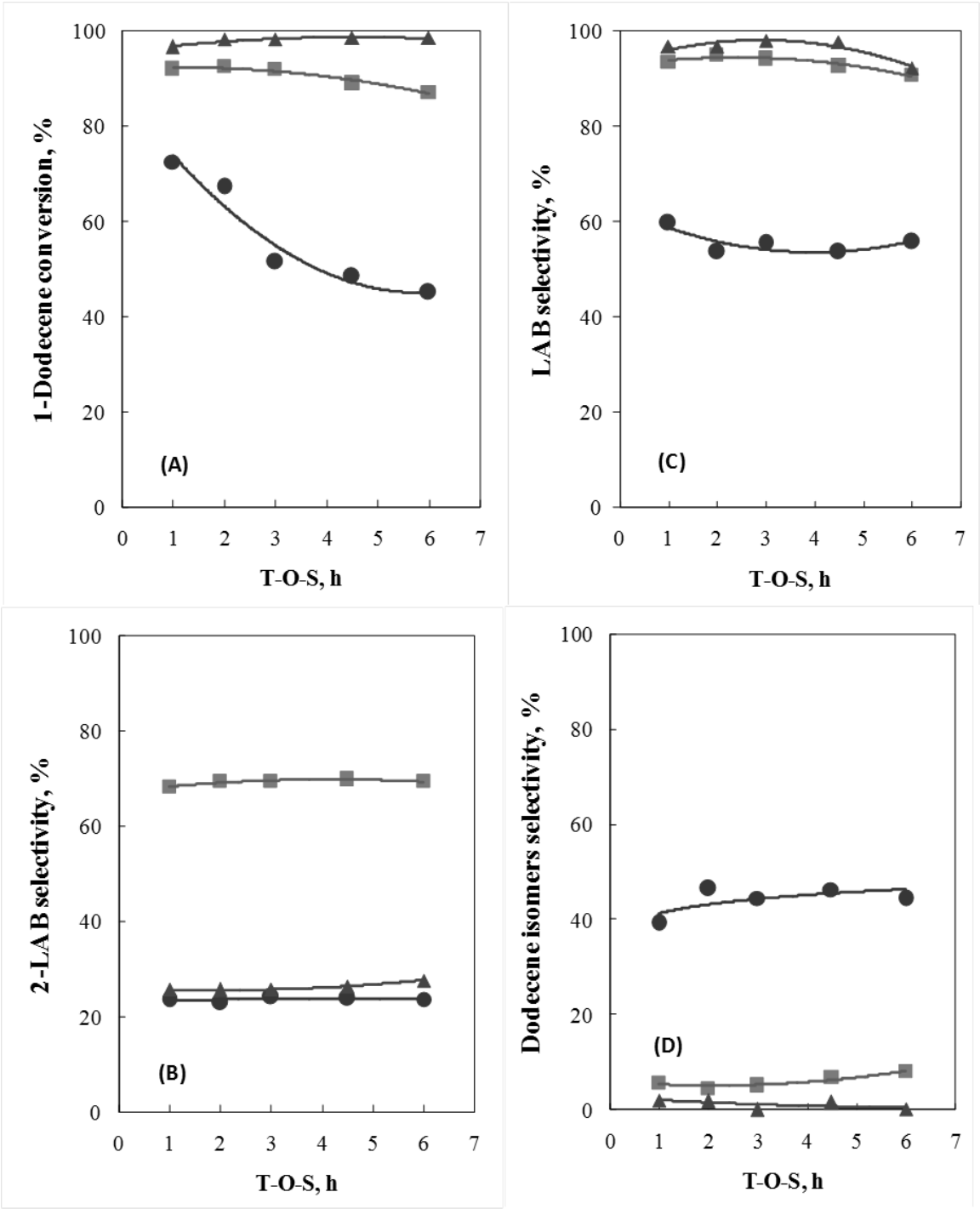



Figure 12: Catalytic performance of parent zeolites (▲USY, ● BEA24, ■ MOR18) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 20 bar, WHSV = 4 $h^{-1}$, benzene: 1-dodecene molar ratio = 6

The conversion of 1-dodecene over the three parent zeolites decreased in the order of: USY > MOR-18 > BEA-24 with constant selectivity to 2-LAB during 6 h of T-O-S. The interaction of 1-dodecene with acid site forms 2-dodecyl carbocation through which double bond isomerization proceeds to form dodecene isomers. The isomers are protonated by acid site to form carbocations which possess positively charged C atom at different positions and attack benzene to form LAB isomers.

The difference in the selectivity to 2-LAB over the three zeolites is influenced by the ability of the individual zeolite active sites in promoting benzene alkylation versus isomerization of 1-dodecene (Table 11 and Fig. 12). Compared with USY, MOR-18 exhibited the selective formation of 2-LAB (68.1%) whereas the selectivity to 3-6 LAB isomers was 71.1% over USY due to its tri-directional network of large cavities and openings [17, 23]. Moreover, the alkylation of benzene to LAB over zeolite catalysts involves the interaction of 1-dodecene with strong acid sites to form 2-dodecylcarbenium ion which undergoes a rapid rearrangement followed by the attack of benzene ring by alkylcarbenium to form LAB isomers [14, 47]. The active sites are either Brønsted acid sites or Lewis acid sites or a combination of them [48]. If both Brønsted and Lewis acid sites are assumed as active sites, the sum of the numbers of these two kinds of acid centers should be responsible for the alkylation activity.

Table 11: Catalytic performance of parent zeolites for benzene alkylation at 140 °C, 20 bar, WHSV = 4 $h^{-1}$, benzene: 1-dodecene molar ratio = 6, 1 h T-O-S

| Parameter | USY | Beta | | Mordenite | |
|---|---|---|---|---|---|
| | | BEA-24 | BEA-40 | MOR-18 | MOR-40 |
| 1-dodecene conversion, % | 96.6 | 72.6 | 81.8 | 92.0 | 77.4 |
| Product Selectivity, % | | | | | |
| Dodecene isomers | 2.0 | 39.2 | 25.4 | 5.7 | 37.9 |
| LAB Isomers | 96.7 | 59.7 | 74.6 | 93.4 | 58.5 |
| > $C_{12}$ HC | 1.3 | 1.1 | 0.0 | 0.9 | 3.6 |
| LAB Isomer Selectivity, % | | | | | |
| 2- LAB | 25.7 | 23.6 | 30.8 | 68.1 | 33.8 |
| 3-6 LAB | 71.1 | 36.1 | 43.8 | 25.3 | 24.7 |
| 2-LAB/3-6 LAB | 0.4 | 0.7 | 0.7 | 2.7 | 1.4 |

### 5.2.2 Effect of desilication

The conversion of 1-dodecene and product selectivity characteristics of parent and desilicated BEA (BEA-24, BEA-40, DBEA-24, DBEA-40) and MOR (MOR-18, MOR-40, DMOR-18, DMOR-40) as a function of T-O-S are presented in Figures 13 and 14 and Table 12. As discussed earlier, alkali-treatment increased the concentration of Lewis acid sites whereas the concentration of Brønsted acid sites decreased (Table 10).

As alkylation is catalyzed by moderate acid sites, higher LAB selectivity in desilicated BEA and MOR zeolites may be attributed to the inhibition of 1-dodecene isomerization. Table 10 shows that the desilication of BEA zeolites resulted in an increase in the

concentration of Lewis acid sites and mesopore volume with a corresponding decrease in both the amount of Brønsted acid sites and micropore volume [49]. The conversion of 1-dodecene over parent zeolite BEA-24 (73%) increased significantly to 98% after desilication to DBEA-24. Selectivity to LABs for BEA-24 increased from 60% to 97% for DBEA-24 while the selectivity to dodecene isomers decreased from 39% to 2% indicating a significant drop in isomerization activity. Similar trend of improved 1-dodecene conversion and selectivity to LAB was observed for BEA-40. The improvement of 1-dodecene conversion and LAB selectivity with T-O-S for desilicated DBEA-40 was more pronounced than the improvement of BEA-24 as shown in Fig. 13. This improvement may be attributed to the presence of mesopores decreasing the real contact time, suppressing as the result the formation of coke precursors and subsequent catalyst deactivation.

Desilication of MOR-18 and MOR-40 resulted in the increase in the 1-dodecene conversion and 2-LAB selectivity, accompanied by significant decrease in the deactivation of MOR-40. 1-Dodecene conversion for both DMOR-18 and DMOR-40 was around 99% after 6 h of T-O-S (Fig. 14). Desilicated DMOR-40 showed a significant increase in the selectivity to 2-LAB from 34% (parent MOR-40) to 60% associated with a drop in the selectivity to dodecene isomers (from 38% to < 2%). The significant increase in 1-dodecene conversion and decrease in the selectivity to dodecene isomers over desilicated DMOR-40 may be attributed to the enhanced porosity after desilication (mesopore volume of DMOR-40 increased from 0.07 $cm^3/g$ to 0.29 $cm^3/g$) [31, 50].

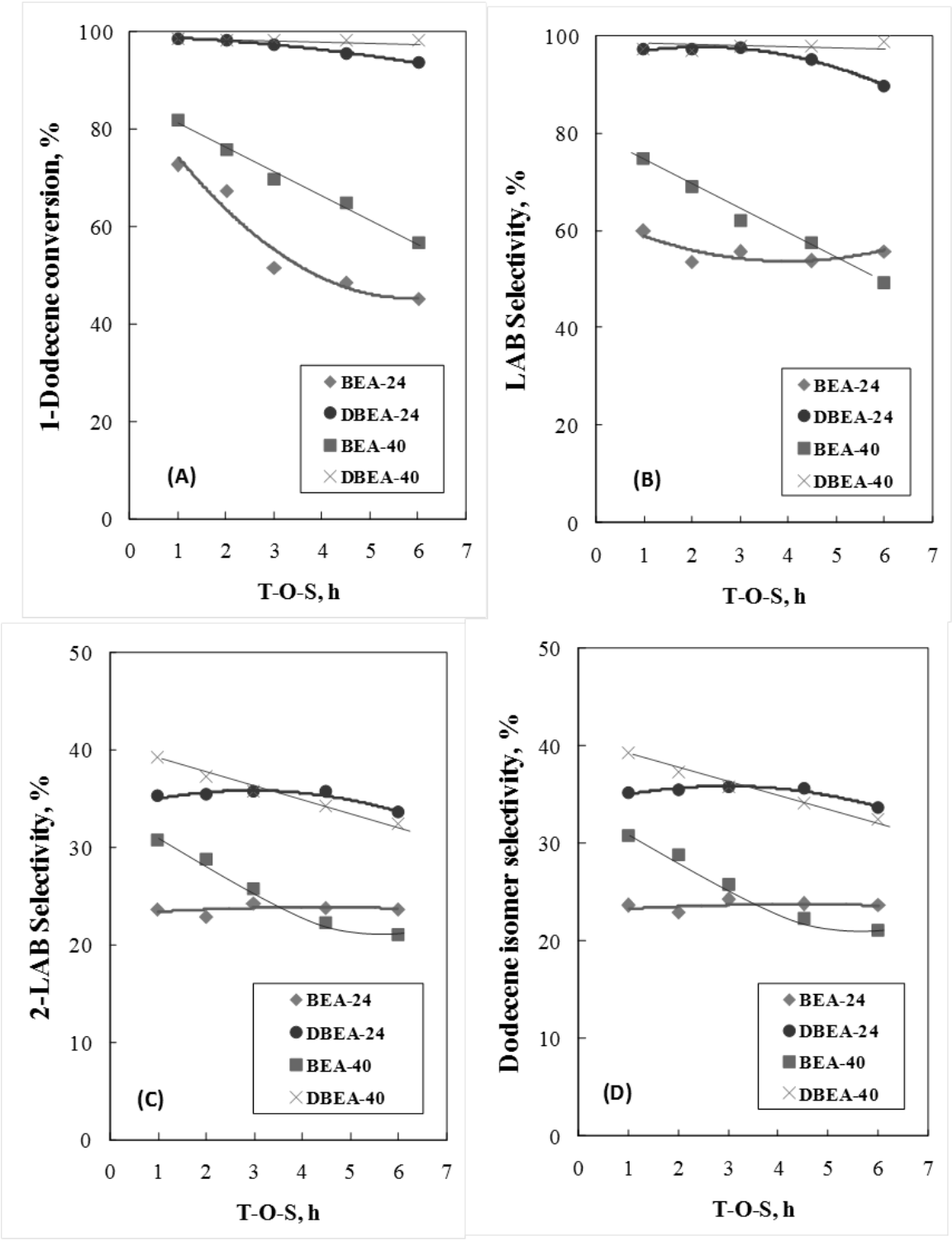



Figure 13: Catalytic performance of parent and desilicated BEA (◊BEA24; ● DBEA24; ■ BEA40; × DBEA40) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 20 bar, WHSV = 4 $h^{-1}$, benzene: 1-dodecene molar ratio = 6

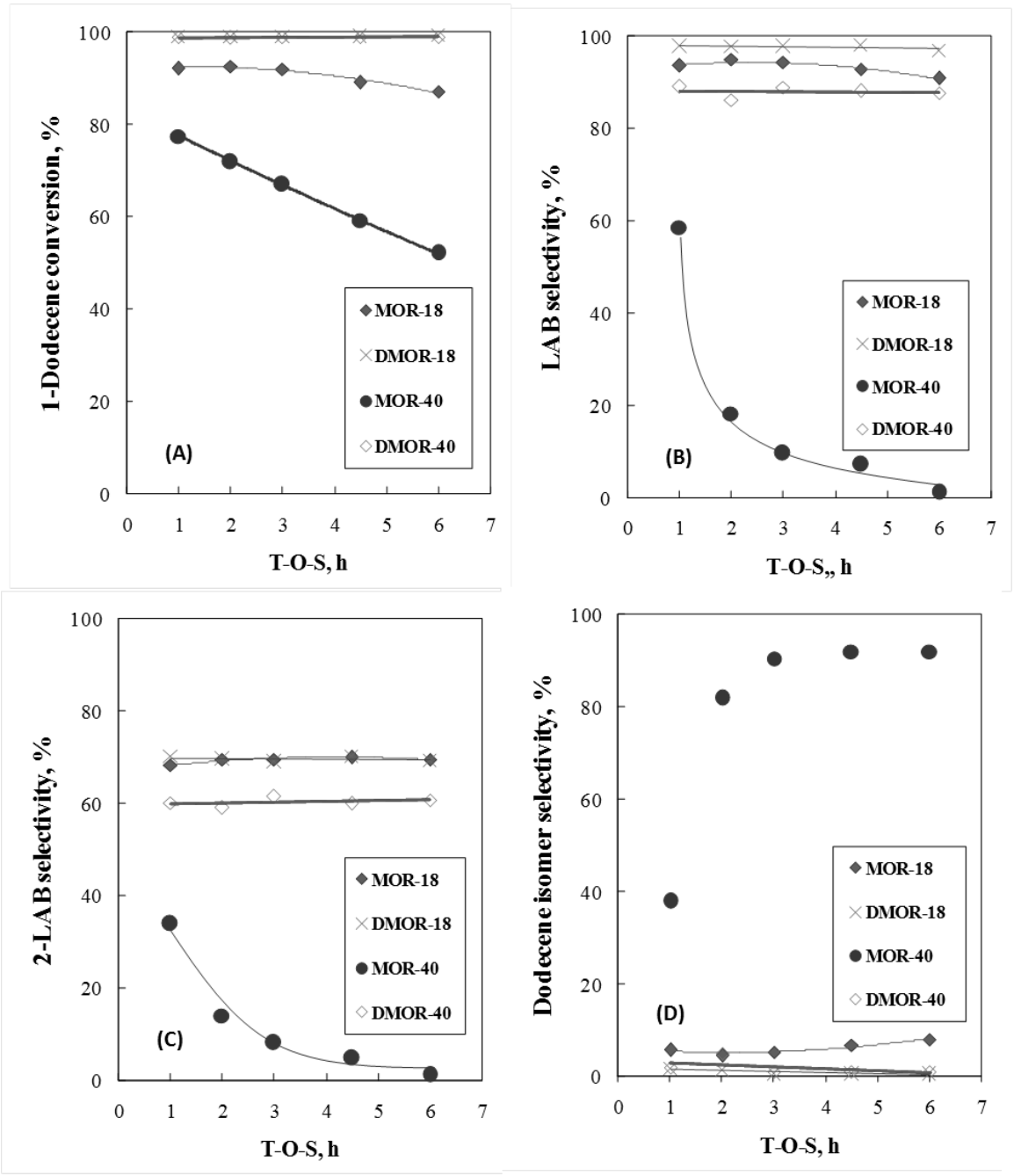



Figure 14: Catalytic performance of parent and desilicated MOR (■ MOR-18; × DMOR-18;● MOR-40; ◊ DMOR-40) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 300 psi, WHSV = 4 $h^{-1}$, benzene: 1-dodecene molar ratio = 6

Table 12: Catalytic performance of parent and desilicated zeolites for benzene alkylation at 140 °C, 20 bar, WHSV = 4 $h^{-1}$, benzene: 1-dodecene molar ratio = 6, 1 h T-O-S

| Parameter | Beta | | | | Mordenite | | | |
|---|---|---|---|---|---|---|---|---|
| | BEA-24 | DBEA-24 | BEA-40 | DBEA-40 | MOR-18 | DMOR-18 | MOR-40 | DMOR-40 |
| 1-dodecene conversion, % | 72.6 | 98.4 | 81.8 | 98.3 | 92.0 | 98.9 | 77.4 | 98.8 |
| Product Selectivity, % | | | | | | | | |
| Dodecene isomers | 39.2 | 2.1 | 25.4 | 2.9 | 5.7 | 0.0 | 37.9 | 1.8 |
| LAB Isomers | 59.7 | 97.1 | 74.6 | 97.1 | 93.4 | 97.8 | 58.5 | 88.2 |
| > $C_{12}$ HC | 1.1 | 0.8 | 0.0 | 0.0 | 0.9 | 2.2 | 3.6 | 10.0 |
| LAB Isomer Selectivity, % | | | | | | | | |
| 2- LAB | 23.6 | 35.2 | 30.8 | 39.3 | 68.1 | 70.0 | 33.8 | 59.6 |
| 3-6 LAB | 36.1 | 61.9 | 43.8 | 57.8 | 25.3 | 27.8 | 24.7 | 28.6 |
| 2-LAB/3-6 LAB | 0.7 | 0.6 | 0.7 | 0.7 | 2.7 | 2.5 | 1.4 | 2.1 |

### 5.2.3 Effect of $SiO_2/Al_2O_3$ ratio

The effect of $SiO_2/Al_2O_3$ ratio on the benzene alkylation was studied using three mordenites (MOR-18, MOR-40, MOR-180) as a function of T-O-S (Fig. 15). In the case of parent MOR samples with varying $SiO_2/Al_2O_3$ ratios (MOR-18, MOR-40, MOR-180), the conversion of 1-dodecene and the selectivity to LAB versus T-O-S are presented in Fig. 15. While the conversion of 1-dodecene over MOR-40 gradually decreased from 77% to 60% during the 6 h of T-O-S, it was nearly constant over MOR-18 (90%) and MOR-180 (99%). After 1 h of T-O-S, the selectivity to 2-LAB was 68% over MOR-18 compared with 54% over MOR-180 and 34% over MOR-40. The selectivity to dodecene isomers over MOR-40 (38%) was the highest, indicating high isomerization activity compared with MOR-18 and MOR-180. The conversion of 1-dodecene and selectivity behavior of MOR-18 and MOR-40 was different compared with beta BEA-24 and BEA-40 which showed increased 1-dodecene conversion and selectivity to 2-LAB with increased $SiO_2/Al_2O_3$ ratio. This behavior of MOR-18 and MOR-40 may be attributed to the differences in the acidity characteristics of these two mordenite samples as shown in Table 10.

MOR-18 exhibited higher concentration of Brønsted acid sites compared with MOR-40 which may explain the high selectivity to dodecene isomers over MOR-40. However, the difference in the concentration of Brønsted acid sites between MOR-18 and MOR-40 is not the only parameter that governs the conversion of 1-dodecene and selectivity to 2-phenyldodecane [23, 51]. Among other factors that may influence 1-dodecene conversion are the diffusion rates (reactants and products) and the possible early deactivation of MOR-40.

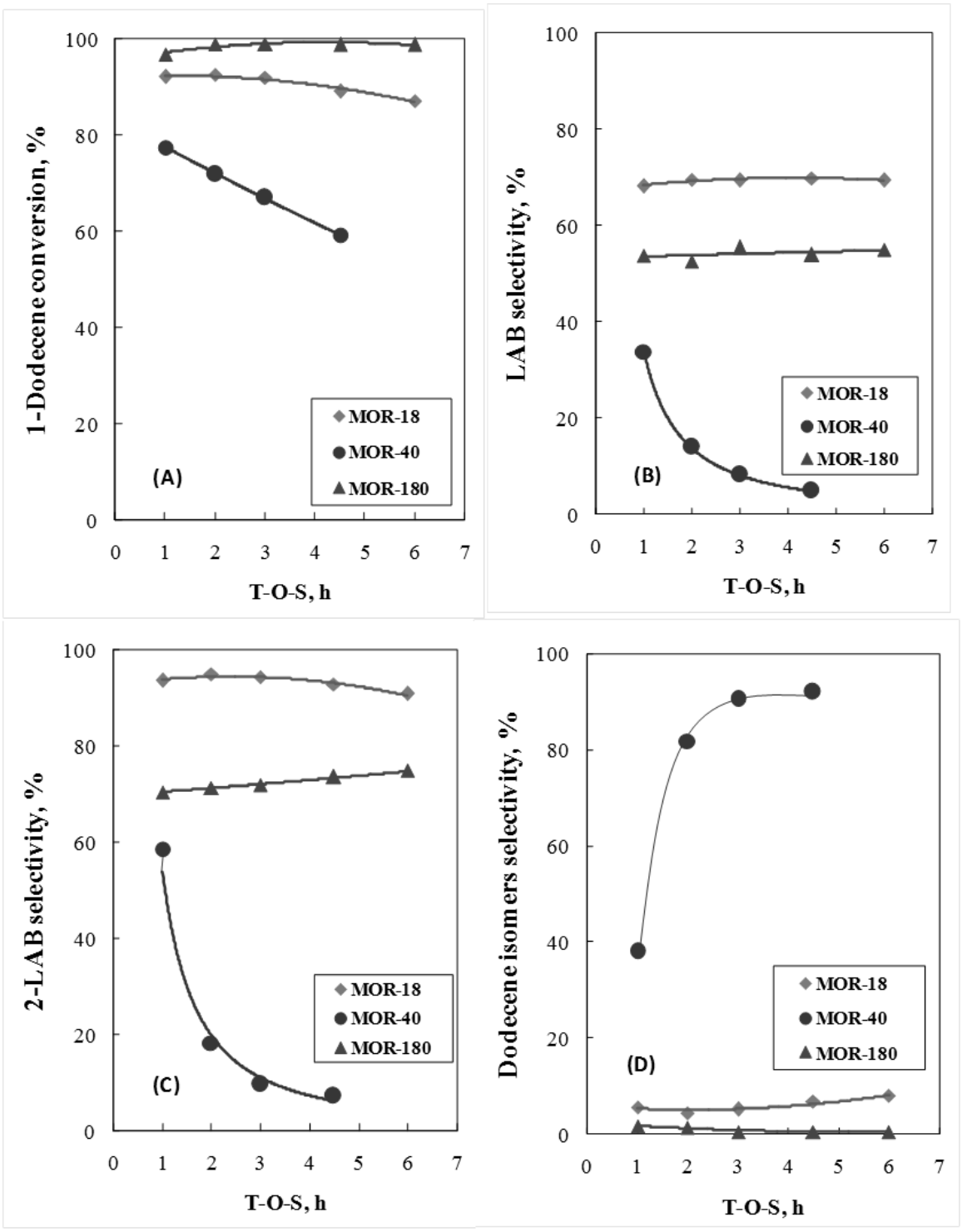



Figure 15: Catalytic performance of parent MOR with different $SiO_2/Al_2O_3$ ratios (◊ MOR18; ● MOR40; ▲ MOR180) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 20 bar, WHSV = 4 $h^{-1}$, benzene: 1-dodecene molar ratio = 6

# CHAPTER 6

# KINETIC STUDIES

## 6.1 Kinetic Studies

From the experimental results we concluded that mordenite with low $SiO_2/Al_2O_3$ ratio gave the maximum conversion of dodecene into linear alkylbenzene isomers and was more selective towards 2-Phenyldodecane [52]. So, to perform kinetic studies we choose a mordenite based catalyst with $SiO_2/Al_2O_3$ = 20, obtained from Zeolyst Chemicals. In addition to its good catalytic performance i.e., 1-dodecene conversion = 98%, LAB isomer selectivity = 96% and 2-phenyldodecane selectivity = 72%, it maintained its good performance for a reasonable period of time, Fig. 16.

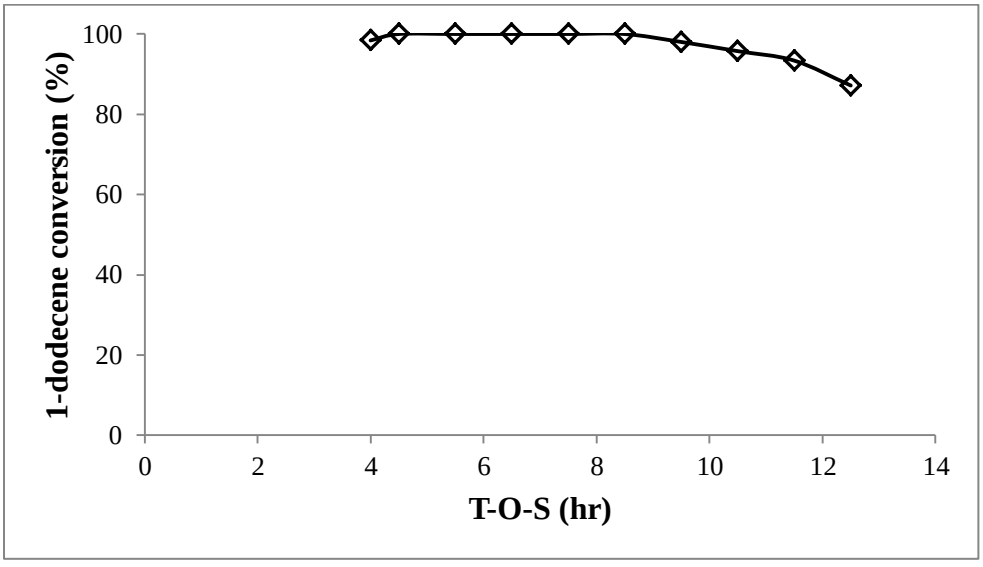



Figure 16: Effect of catalyst (MOR-20) aging on % Conversion of dodecene

For the development and optimization of industrial processes a detailed knowledge of involved chemical reactions is indispensible. A good kinetic model helps in deciding the best operating conditions and tailoring a catalyst with desirable characteristics. Tsai et al have developed a kinetic model assuming pseudo first order kinetics for benzene alkylation with dodecene using mordenite [37]. They reported activation energy of 17 kCal/mol (71.06 kJ/mol) using benzene in excess and dodecene as limiting reactant. Yadav and Doshi have studied alkylation kinetics over non-zeolytic catalysts [2]. Jinchang Zhang et al have suggested carbenioum ion mechanism for benzene alkylation with 1-dodecene over supported tungstophosphoric acid catalyst [53]. Unfortunately, most of the kinetic models available in literature do not describe double bond isomerization and benzene alkylation simultaneously. Ionel and coworkers [54] presented an effective model depicting the alkylation of benzene with octenes over Y Zeolites. The present study covers the complete reaction network including dodecene isomerization occurring in parallel with the benzene alkylation reactions over mordenite. The power law models considered are established based on extensive set of kinetic experiments using a fixed bed flow type reactor. The various reactions parameters are estimated from the proposed kinetic model by least-square fittings of the model equation using experimental data implemented in MATLAB. The estimated parameters are evaluated based on their physical significances and various statistical indicators. However, for each run 'fresh catalyst' was used so this model do not account for the catalyst deactivation with time.

## 6.2 Experimental details

### 6.2.1 Chemicals and catalysts:

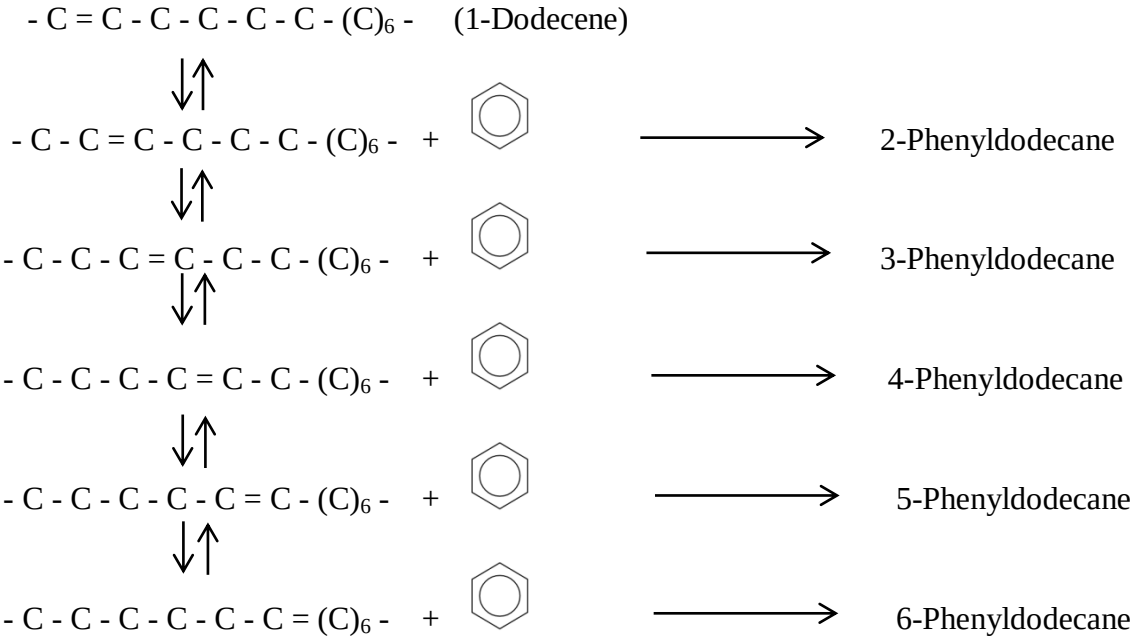
Commercial mordenite sample CBV-21 ($SiO_2/Al_2O_3$ = 20) was obtained from Zeolyst Chemicals. Research grade benzene and dodecene were procured from Sigma-Aldrich Chemicals. Alumina balls of size 0.1mm were used as inert packing of the catalyst bed.

### 6.2.2 Catalyst testing:

A 5 ml tubular reactor (BTRS-Jr) provided by Autoclave Engineers was used to study the kinetics of alkylation reaction. A 6:1M mixture of benzene and dodecene was introduced into the reaction system using a positive displacement pump at a flow rate of 0.08 ml/min. Reaction temperature was varied between 80 °C to 140 °C. Nitrogen was introduced with the feed, as a carrier gas, at a flow-rate of 50 ml/min. The flow rate of the feed was high enough to overcome any diffusional limitations. Catalyst was sieved to a particle size of 0.5 to 1 mm. Different weights of catalyst sample (MOR-20) were loaded in the reactor i.e., alkylation reaction was carried out at different space times to have different degrees of conversion. The product analysis was carried out in GC-FID (Agilent 7890) and GC-MS (Agilent 5980).

## 6.3 General sequence of reaction

The synthesis of linear alkylbenzenes proceeds with a combination of double bond isomerization of 1-Dodecene followed by alkylation.



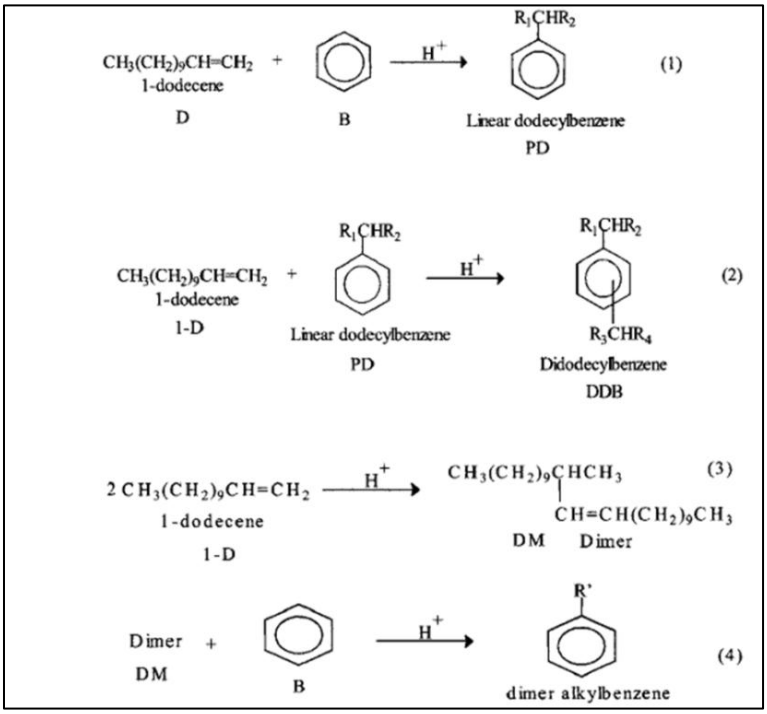




Figure 17: Possible side reactions during alkylation of Benzene with 1-dodecene [2]

## 6.4 Product analysis and reaction scheme

As mentioned in the experimental section, the alkylation was carried out using a fixed bed reactor with 6:1 molar ratio of benzene to 1-dodecene. The reaction temperature was varied between 80 °C to 140 °C at different contact times. For each experiment the product was analyzed. The analysis data was further processed to determine conversion and product selectivity. Table 13 displays the product analysis results of alkylation of benzene with 1-dodecene at different reaction conditions. One can see from Table 13 that the main products are the 2-, 3- isomers of dodecene and 2-, 3-phenyldodecane. Under the reaction conditions no dialkylated products were observed even at higher reaction temperature of 140 °C. This was due to the presence of excess benzene in the reaction mixture. For all the studied experimental conditions the concentrations of higher isomers of linear alkylbenzene 4-,5- and 6-phenyldodecanes were also negligible.

Fig. 18 highlights the effects of temperature on conversion of 1-dodecene and selectivity of linear alkylbenzene isomers at a specific space time (4.92 min.).

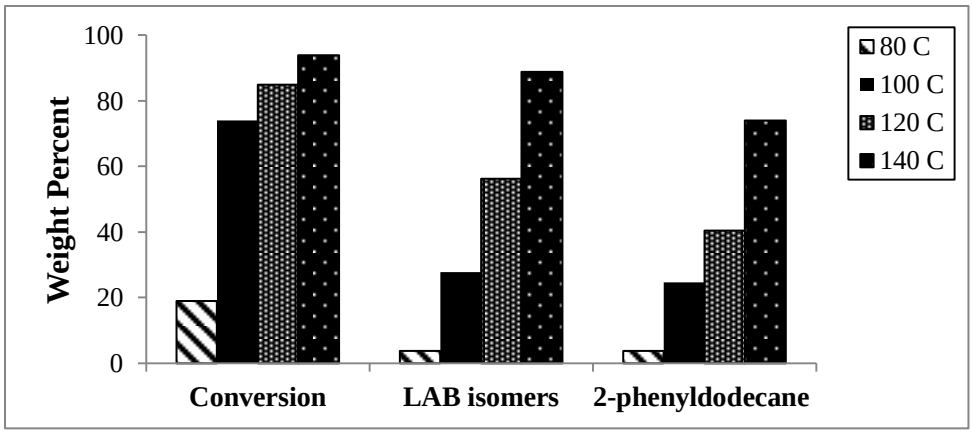



Figure 18: Effect of temperature on conversion and selectivity of LAB isomers

At low temperature (80 °C), the conversion of 1-dodecene was approximately 20 %. The selectivity of both the LAB isomers and 2-phenyldodecane are also marginal at this temperature level. When the temperature was increased to 100 °C, the 1-dodecene conversion jumped to 75 % level, producing significant amount of LAB isomers and 2-phenyldodecane. Above 100 °C, both the 1-dodecene conversion and product selectivity (LAB isomers and 2-phenyldodecane) almost linearly increased with the increase of reaction temperature.

The effects of space time on the 1-dodecene conversion at various temperature levels are shown in Fig. 19. Again at low temperature and short contact time the conversion of 1-dodecene was very low. No significant increase was observed with the increase of space time. Contrarily, at reaction temperatures above 100 °C, 1-dodecene conversion first linearly increased closed to the highest value, after that no significant increment was observed with the increase of space time. At higher temperature, the maximum 1-dodecene conversion was achieved comparatively at smaller space time. Previous studies also reported similar observation using different catalysts [1, 2, 53 and 54]. Yadav and Doshi [2] have studied the effect of benzene/1-dodecene mole ratio over alkylation reaction and reported that for 1-dodecene to benzene mole ratio of 1:2 didodecylbenzene was formed. Keeping in mind, in this study benzene was used in excess in order to avoid the formation of the by-products.

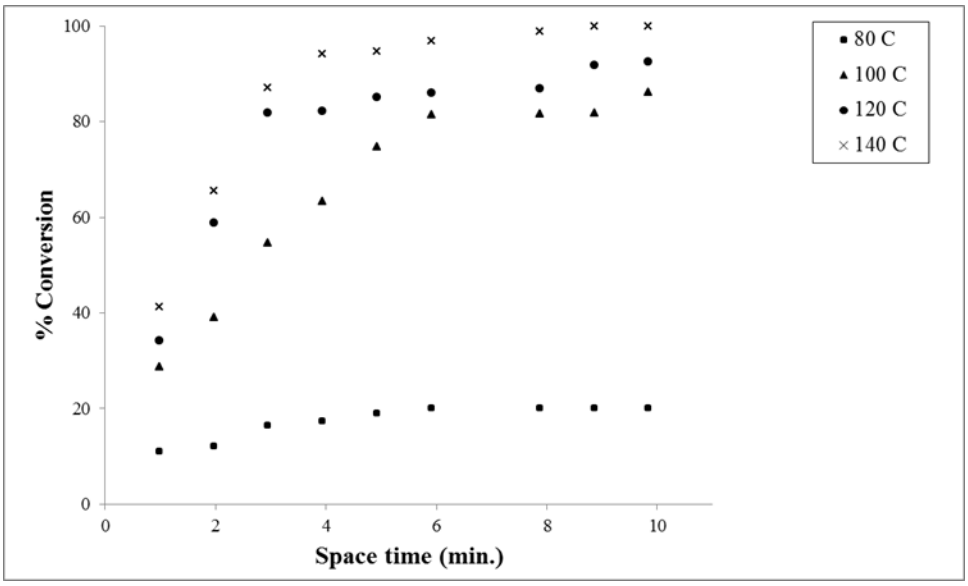



Figure 19: Effect of temperature and contact time on % Conversion of 1-dodecene

Fig. 20 plots the selectivity of different products at various space time and different temperature levels. One can see that at low temperature of 80 °C, 2-phenyldodecane was the only LAB isomer observed and even at the highest space time of 9.84 min. The selectivity of LAB isomers was less than 10% and most of the 1-dodecene remained unconverted as seen in Fig. 20. At 100 °C, alkylation reaction took place considerably and the reaction products become more selective towards 2-phenyl isomer. In addition to this, with the increase in space time above 4 minutes, small amounts of 3-phenyldodecane were also found in the reaction products. Further increase in reaction temperature to 120 and then to 140 °C, the selectivity to LAB isomers increased to 90% for larger space times and significant amounts of 3-phenyldodecane were observed in the reaction products while 2-phenyldodecane was still being the most selective isomer. The higher 2-phenyldodecane selectivity of mordenite is believed to be due to the narrow pore opening of the catalysts which restricts the formation/diffusion of bulky molecule in the

pore channels [37]. Da et al [55] reported that 2-phenyl isomer of LAB diffuses easily than other isomers. Therefore, the isomer selectivity can be attributed to the "product shape selectivity", which is controlled by the diffusion resistances imposed by the pore size of the zeolite. In addition to this, LAB production reaction is a combination of double bond migration followed by benzene alkylation, the relative rate ratio of alkylation reaction to double bond migration determines linear alkylbenzene isomer selectivity. In general, the greater the ratio of alkylation to double bond migration more selective is the reaction towards 2-phenyldodecane [37]. Cao et al [23] have proposed that in a LAB production reaction, dodecene forms a carbenium ion over acid catalyst, then undergoes a rapid double bond migration and finally alkylates benzene.

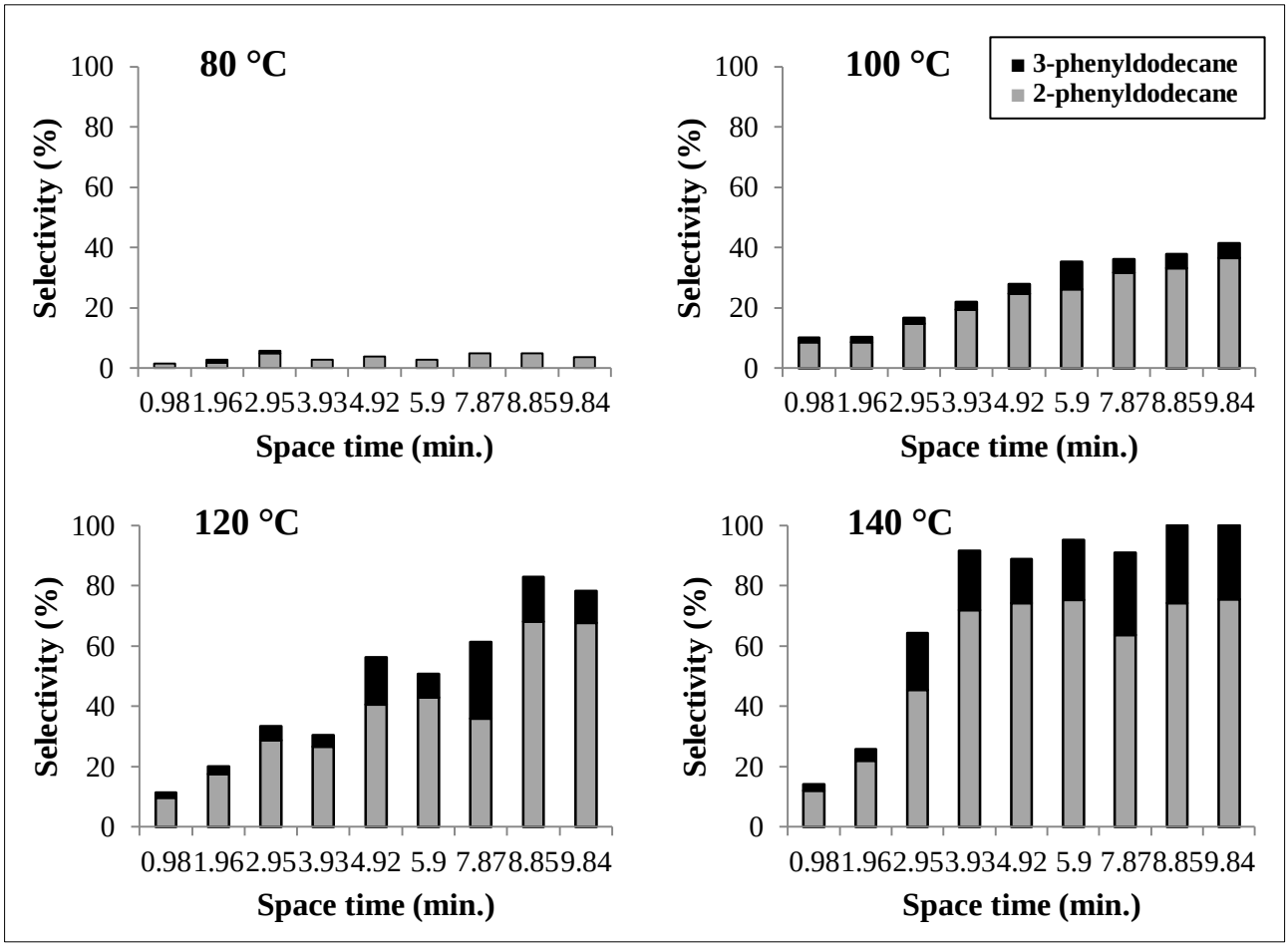



Figure 20: Effect of temperature and space time on selectivity of LAB isomers

Fig. 21 compares the selectivity of dodecene isomers at various space time and different temperature levels. At the lowest temperatures (80 °C) the maximum selectivity of dodecene isomers was 10%. With low space times of 0.98 and 1.96 minutes, the double bond isomerization of dodecene took place significantly and selectivity of dodecene isomers was 32% at 140 °C. However, with the increase in space time above 4 minutes, dodecene isomers readily alkylated to corresponding LAB isomers at 140 °C and amounts of dodecene isomers observed were negligible (Fig. 21 d). A similar trend in the selectivity of dodecene isomers was observed at 120 °C as depicted by Fig. 21 c. At higher space times of 8.85 and 9.84 minutes, the dodecene isomers were completely consumed in alkylation reaction to form 2 and 3-phenyldodecanes. However, at 100 °C, dodecene isomers did not react with benzene and as a result the selectivity of dodecene isomers was the highest (38%) at 100 °C even for the longest contact time of 9.84 minutes in the reactor (Fig.21 b). Therefore, under the studied reaction conditions the amount of unreacted 3-dodecene is more which confirms that 2-dodecyl carbenium ion alkylate benzene into corresponding LAB isomer more readily than any adjacent dodecyl carbenium ion [37].

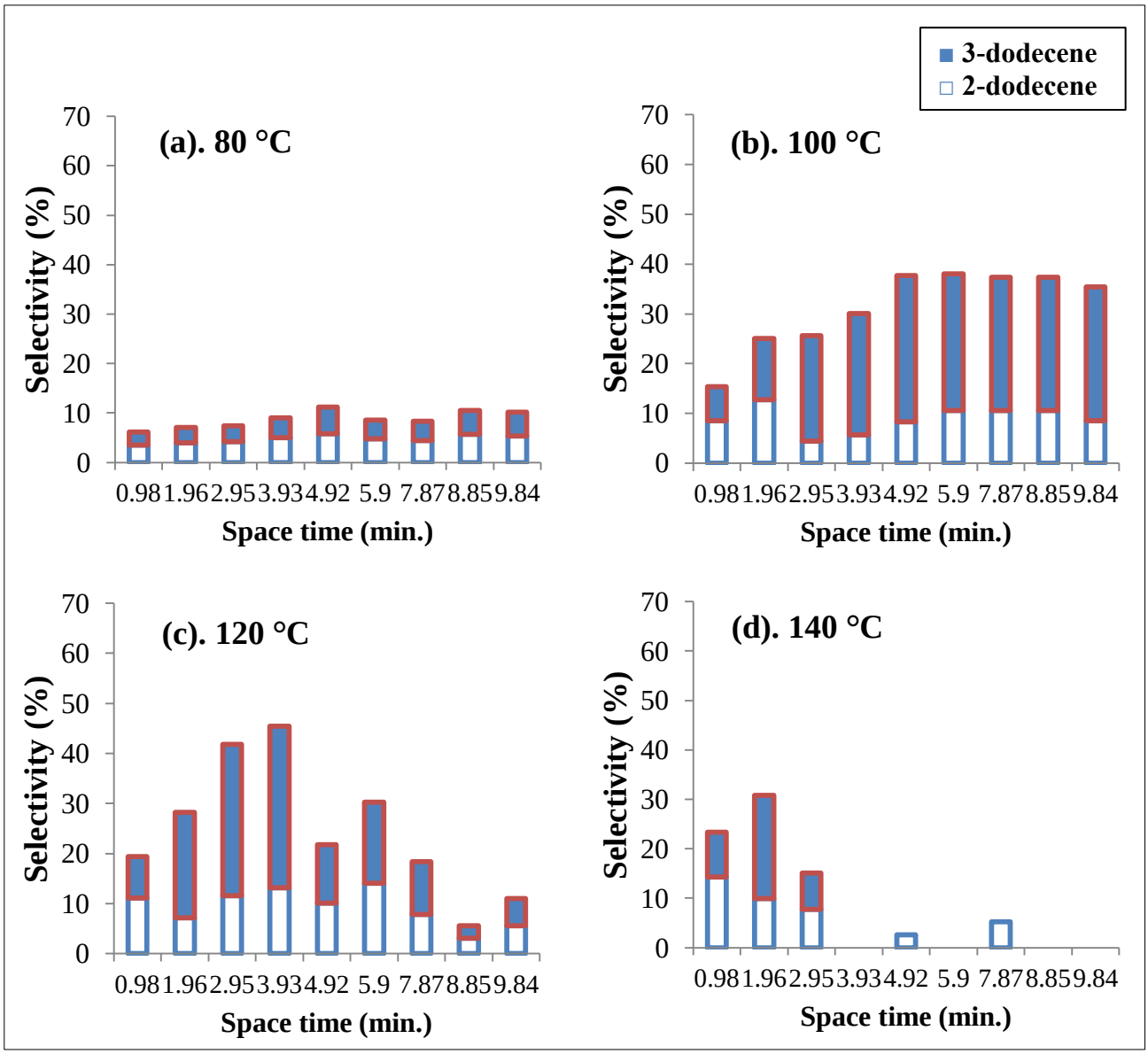
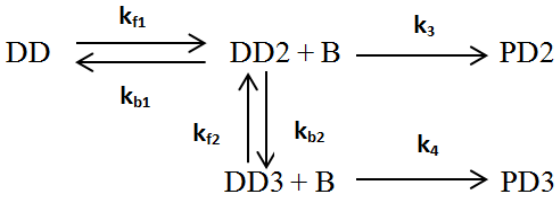



Figure 21: Effect of temperature and selectivity of dodecene isomers

Based on the above discussion, one can conclude that under the studied reaction conditions MOR-20 is more selective towards 2 and 3-phenyldodecane and the amount of higher LAB isomers can be considered negligible (Table 13). In addition to this, using benzene to dodecene molar ratio 6:1 the undesired products such as didodecylbenzene, dimer of dodecene, dimer alkylbenzene were not observed in the reaction products. Considering all the facts the reaction Scheme -1 (below) has been proposed and subsequently considered for the kinetics modeling.




Scheme 1.Reaction network of alkylation of benzene with 1-dodecene
*(B: Benzene; DD:Dodecene; DD2:2-Dodecene; DD3:3-Dodecene; PD2:2-Phenyldodecane; PD3:3-Phenyldodecane)*

Table 13: Yield data at 80, 100, 120 & 140 °C

| Temperature | Space time (min.) | 1-dodecene conversion (%) | Concentration of products | | | |
|---|---|---|---|---|---|---|
| | | | 2-dodecene ($mmol/cm^3$) | 3-dodecene ($mmol/cm^3$) | 2-phenyldodecane ($mmol/cm^3$) | 3-phenyldodecane ($mmol/cm^3$) |
| 80 °C | | | | | | |
| | 0.98 | 11.00 | 0.16 | 0.13 | 0.08 | 0 |
| | 1.96 | 12.14 | 0.19 | 0.15 | 0.08 | 0.05 |
| | 2.95 | 16.50 | 0.20 | 0.15 | 0.23 | 0.04 |
| | 3.93 | 17.31 | 0.23 | 0.19 | 0.13 | 0 |
| | 4.92 | 19.00 | 0.28 | 0.25 | 0.18 | 0 |
| | 5.90 | 20.00 | 0.21 | 0.17 | 0.13 | 0 |
| | 7.87 | 20.00 | 0.20 | 0.18 | 0.23 | 0 |
| | 8.85 | 20.00 | 0.27 | 0.22 | 0.24 | 0 |
| | 9.84 | 20.00 | 0.25 | 0.22 | 0.17 | 0 |
| 100 °C | | | | | | |
| | 0.98 | 28.73 | 0.41 | 0.33 | 0.41 | 0.07 |
| | 1.96 | 39.16 | 0.61 | 0.58 | 0.41 | 0.08 |
| | 2.95 | 54.70 | 0.18 | 0.84 | 0.59 | 0.07 |
| | 3.93 | 63.43 | 0.22 | 0.93 | 0.74 | 0.09 |
| | 4.92 | 74.83 | 0.31 | 1.08 | 0.91 | 0.12 |
| | 5.90 | 81.50 | 0.37 | 0.96 | 0.92 | 0.32 |
| | 7.87 | 81.70 | 0.37 | 0.93 | 1.10 | 0.16 |
| | 8.85 | 81.80 | 0.39 | 0.99 | 1.23 | 0.17 |
| | 9.84 | 86.20 | 0.26 | 0.81 | 1.10 | 0.15 |
| 120 °C | | | | | | |
| | 0.98 | 34.20 | 0.53 | 0.39 | 0.47 | 0.07 |
| | 1.96 | 58.76 | 0.28 | 0.85 | 0.70 | 0.10 |
| | 2.95 | 81.75 | 0.42 | 1.12 | 1.07 | 0.16 |
| | 3.93 | 82.20 | 0.49 | 1.20 | 0.99 | 0.14 |
| | 4.92 | 85.10 | 0.34 | 0.39 | 1.38 | 0.54 |
| | 5.90 | 86.00 | 0.52 | 0.60 | 1.60 | 0.29 |
| | 7.87 | 86.81 | 0.25 | 0.34 | 1.17 | 0.83 |
| | 8.85 | 91.71 | 0.11 | 0.091 | 2.47 | 0.53 |
| | 9.84 | 92.57 | 0.19 | 0.18 | 2.34 | 0.36 |
| 140 °C | | | | | | |
| | 0.98 | 41.30 | 0.68 | 0.43 | 0.57 | 0.09 |
| | 1.96 | 65.50 | 0.39 | 0.83 | 0.88 | 0.15 |
| | 2.95 | 87.00 | 0.24 | 0.23 | 1.45 | 0.60 |
| | 3.93 | 94.18 | 0 | 0 | 2.49 | 0.68 |
| | 4.92 | 94.60 | 0.08 | 0 | 2.39 | 0.47 |
| | 5.90 | 96.83 | 0 | 0 | 2.54 | 0.67 |
| | 7.87 | 98.80 | 0.08 | 0 | 1.03 | 0.44 |
| | 8.85 | 100 | 0 | 0 | 2.65 | 0.72 |
| | 9.84 | 100 | 0 | 0 | 2.46 | 0.20 |

## 6.5 Kinetics modeling

In this section the details kinetics of alkylation of benzene with 1-dodecene over mordenite ($SiO_2/Al_2O_3$ = 20) are described. The present model describes the double-bond isomerization of 1-dodecene occurring in parallel with alkylation of benzene. The reaction rate equations are developed based on power law models. The model formulation considered that the double bond isomerization of 1-dodecene follows a 'reversible path' while alkylation reaction follows 'irreversible path'; there is no de-alkylation [54]. Further, the mole balance of reactant and product species during the alkylation of benzene in the 'Fixed bed reactor' provides the direct relation among the intrinsic reaction rates of the individual reaction steps and the concentrations of involved species:

i. Net rate of disappearance of 1-dodecene:

$$\frac{dC_{DD}}{d\tau} = -k_{f1}\left(C_{DD} - \frac{C_{DD2}}{K_{eq.1}}\right)$$

***ii.*** Net rate of formation of 2-dodecene:

$$\frac{dC_{DD2}}{d\tau} = k_{f1}\left(C_{DD} - \frac{C_{DD2}}{K_{eq.1}}\right) - k_{f2}\left(C_{DD2} - \frac{C_{DD3}}{K_{eq.2}}\right) - k_3 C_{DD2}$$

***iii.*** Net rate of appearance of 3-dodecene:

$$\frac{dC_{DD3}}{d\tau} = k_{f2}\left(C_{DD2} - \frac{C_{DD3}}{K_{eq.2}}\right) - k_4 C_{DD3}$$

***iv.*** Rate of formation of 2-phenyldodecane:

$$\frac{dC_{PD2}}{d\tau} = k_3 C_{DD2}$$

***v.*** Rate of formation of 3-phenyldodecane:

$$\frac{dC_{PD3}}{d\tau} = k_4 C_{DD3}$$

Where,

$\tau$ = Space time (min.).

$C_{xx}$ = Concentration of the reacting species/products (mmol/ml).

k = rate constants (ml/g-min.)

keq = Equilibrium constant for dodecene isomerization.

## 6.6 Model assumptions:

In model formulation the following assumptions were considered:

**a)** The alkylation of benzene with dodecene was considered to be 'Pseudo first order' i.e., benzene is in excess with respect to dodecene (Benzene to dodecene molar ratio is 6:1) so change in concentration of benzene is negligible during the reaction and rate of reaction depends only on the concentration of 1-dodecene.

**b)** No formation of higher LAB isomers i.e., 4, 5 and 6-phenyldodecane and other byproducts during the alkylation reaction.

**c)** Each time fresh catalyst was used so catalyst deactivation and coke formation over the catalyst surface is negligible.

**d)** The reactor operates under isothermal condition which is justified by the negligible temperature change observed during the reaction.

**e)** Double bond isomerization of 1-dodecene follows a 'reversible path' while alkylation reaction follows 'irreversible path' i.e., there is no de-alkylation. This

assumption is also justified by the study of Ionel et al [54], who studied alkylation of benzene with 1-octene over Y-Zeolite and reported activation energy of 222 $kJmol^{-1}$ for de-alkylation which is much higher as compared with the activation energies of other elementary steps.

## 6.7 Calculation of equilibrium constant

During the course of alkylation of Benzene with 1-dodecene, in the presence of an acidic catalyst, 1-dodecene isomerizes to 2-dodecene. This 2-dodecene is further isomerized to 3-dodecene. This double bond isomerization of the Olefin is considered to be 'reversible reaction' as predicted by Ionel et al [54] for alkylation of Benzene with 1-octene over Y-Zeolite. In our reaction scheme we have followed the same reversible reaction path for double bond isomerization of dodecene. The equilibrium constant for the reversible double bond isomerization of 1-dodecene to 2 and 2 to 3-dodecene can be estimated in the form of Enthalpy ($\Delta H^{\circ}$) and Entropy ($\Delta S°$) of elementary reaction steps, using the Thermodynamic equations 1 and 2 [56].

$$1.\quad K_{eq} = \mathbf{K^{\circ}_{rep}} \times \exp\left[\frac{-\Delta H^{\circ}}{R} \times \left[\frac{1}{T} - \frac{1}{T_m}\right]\right]$$

$$2.\quad K^{\circ}_{rep} = \exp\left[\frac{\Delta S^{0}}{R}\right] \times \exp\left[\frac{-\Delta H^{\circ}}{R \times T_m}\right]$$

Where,

R = 8.314 J/mol-K

$T_m$ = 373 K

Table 14: Reaction Enthalpy and Entropy for double bond isomerization of Olefins [54]

| **Elementary reaction step** | **Reaction Enthalpy, ΔH° (kJ/mol)** | **Reaction Entropy, ΔS° ($J\text{-}mol^{-1}.\ K^{-1}$)** |
|---|---|---|
| 1-dodecene to 2-dodecene | -32.5 | -133.6 |
| 2-dodecene to 3-dodecene | -25.9 | -125.2 |

## 6.8 Parameter estimation

The mole balance equations incorporating with Power law models for the individual reaction steps, Arrhenius relation and the temperature dependence form of the equilibrium constants, were evaluated by a least-squares fitting of the kinetic parameters using the experimental data for benzene alkylation reaction obtained from the packed bed reactor. The differential equations were solved by Runge−Kutta method (MATLAB ODE 45subroutine). On the other hand, the Modified Marquadmethod technique (MATLAB LSQCURVEFIT subroutine) was employed for parameter estimation. In order to ensure reliable model parameter estimation, the catalytic alkylation of benzene with 1-dodecene experiments were conducted at wide range of reaction temperatures (80 to 140 °C) and various space times. In this fashion total one hundred and eighty (180) data points were obtained and used in parameter estimation. Therefore, eight kinetics parameters were determined with a degree of freedom of 172 (degree of freedom = No of experimental data points – No of model parameters). The sufficient numbers of experimental data points obtained/used in parameter estimation provides reliability of the model parameter.

To avoid strong binary correlations, a reparameterization is applied to the Arrhenius equation to center the data around a reference temperature, $T_m$ (100 °C), rather than $T_{infinity}$ [57].

$$\mathbf{k} = \mathbf{k_0} \times \mathbf{exp}\left[\frac{-\mathbf{E_a}}{\mathbf{R}}\left(\frac{\mathbf{1}}{\mathbf{T}} - \frac{\mathbf{1}}{\mathbf{T_m}}\right)\right]$$

The optimization criteria for the model evaluation are that all the rate constants, equilibrium constants, the activation energies, and the frequency factor have to be positive, all consistent with physical principles. The minimum sum of squares of the residuals was set as optimization criterion which was defined by:

$$SS = \sqrt{\sum_{i=1}^{N}(C_{i,\ exp} - C_{i,\ pre})^2}$$

Fig.22 shows the comparison between the experimental and model predicted conversion of 1-dodecene and 2-phenyldodecane. One can see in these plots, model predictions compared favorably with experimental data with only few exceptions.

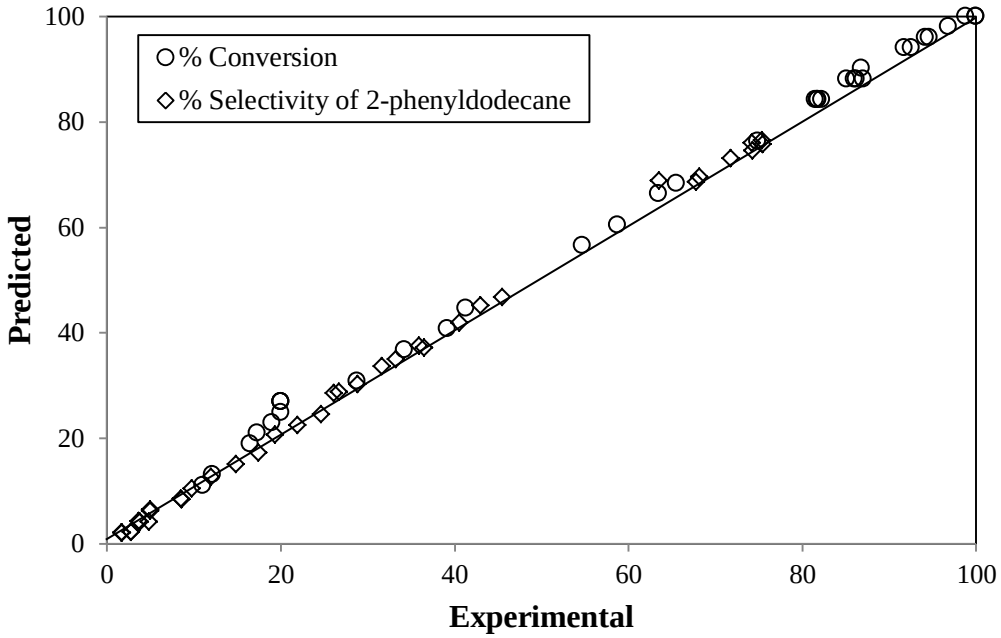



Figure 22: Reconciliation plot between model predictions and experimental data

Fig. 23 shows the Arrhenius plots of various specific reaction rate constants. The straight line with negative slopes of all the Arrhenius plots (as shown in Fig.23) of the rate constants confirms the thermodynamic consistency of the present Power Law model.

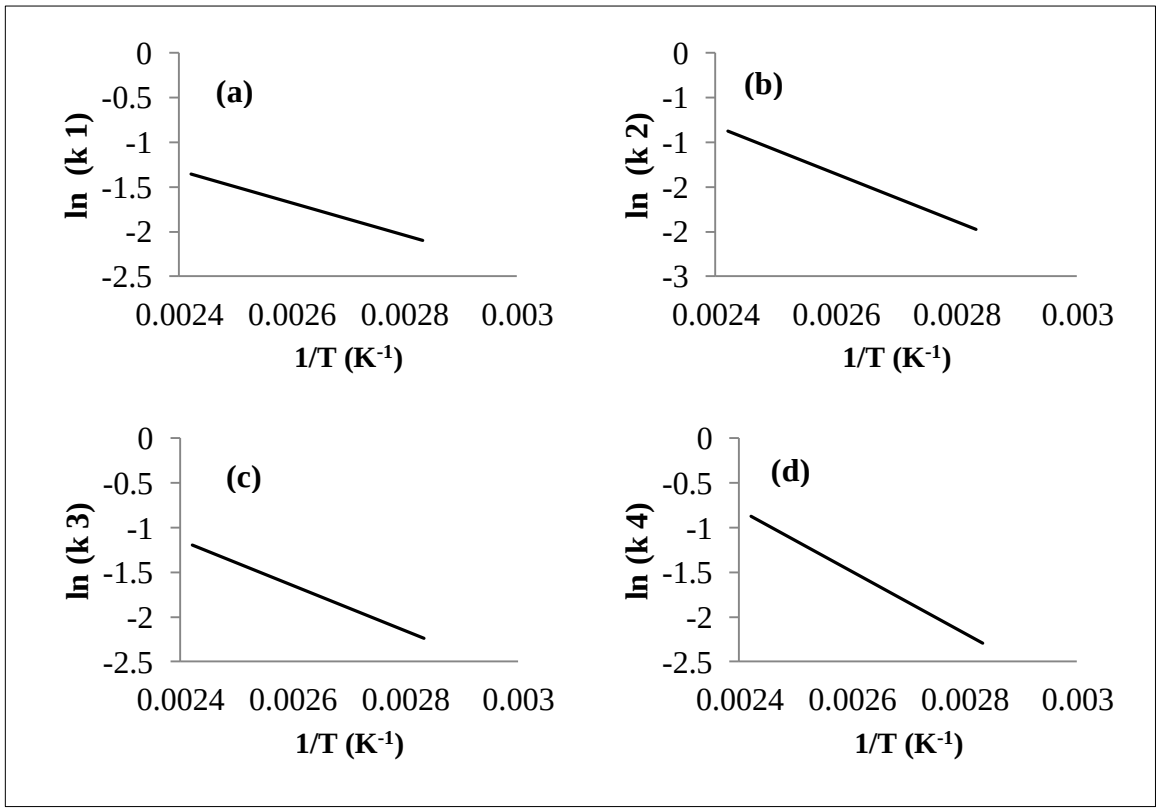



Figure 23: Arrhenius plots for double bond isomerization of (a) 1-dodecene to 2-dodecene (b) 2-dodecene to3-dodecene and alkylation of benzene to (c) 2-phenyldodecane (d) 3-phenyldodecane

Table 15 presents the estimated kinetic parameters for each elementary step in the alkylation reaction of benzene with dodecene.

Table 15: Estimated Activation energy (kJ/mol) and frequncy factor ($m^3$/mol-sec) for each elemantary step during alkylation reaction

| **Elementary reaction step** | **$k_o$** ($m^3$/mol – sec) | **$E_a$** (kJ/mol) |
|---|---|---|
| **1-dodecene to 2-dodecene** | 0.15±0.0002 | 34.5±5.88 |
| **2-dodcene to 3-dodecene** | 0.027±0.001 | 51.1±19.53 |
| **2-dodecene + Benzene = 2-Phenyldodecane** | 0.014±0.0008 | 48.5±32.65 |
| **3-dodecene + Benzene = 3-Phenyldodecane** | 0.017±0.0004 | 66±12.76 |

## 6.9 Comparison with literature

The activation energy of 34.5 kJ/mol was obtained for the isomerization of 1-dodecne to 2-dodecene whereas the for double bond isomerization of 2-dodecne to 3-dodecne the activation energy obtained was 51.1 kJ/mol. These estimated values are in agreement with the ones reported by Ionel et al [54] for double bond isomerization of 1-octene over Y-Zeolite, who reported activation energy of 46 kJ/mol for olefin protonation. However, Jeffrey C. Gee and Shawn Williams [58] studied the competitive double bond isomerization kinetics of 1-dodecene over Amberlyst® 15 and reported that 1-dodecene isomerized to 2-dodecene about 1.9 times faster than the internal dodecne isomerized to adjacent internal olefins so this fact accounts for the much less activation energy of 34.5 kJ/mol for double bond isomerization of 1-dodecene to 2-dodecene as compared to the activation energy of 51.1 kJ/mol for double bond isomerization of 2 to 3-dodecene. The alkylation of benzene to 2-phenyldodecane and 3-phenyldodecane is accompanied with estimated activation energies of 48.5 kJ/mol and 66 kJ/mol respectively. These estimated values of activation energy are much similar with the composite activation energy of 71 kJ/mol, reported by Tsai et al [37] for alkylation reaction of benzene with dodecene over mordenite. It is evident from the yield data that MOR-20 is more selective towards 2-phenyldodecane and the amount of other LAB isomers are less than 2-PD. This fact also supports the lower activation energy for 2-phenyldodecane formation.

# CHAPTER 7

# CONCLUSIONS

The main conclusions from the study of different zeolites for alkylation reaction can be summarized as follows:

1. Conversion of 1-dodecene and the selectivities to 2-phenyldodecane over zeolites FAU, BEA, MOR and their desilicated analogues are controlled by zeolite pore structure.

2. Although FAU zeolite exhibited the high conversion of 1-dodecene (96%), but it was the least selective towards 2-phenyldodecane due to its three-dimensional channel system with large cavities.

3. Zeolite BEA showed the highest selectivity (39.2%) towards dodecene isomers.

4. The effect of varying $SiO_2/Al_2O_3$ ratio for mordenite revealed that catalytic performance is improved (higher 1-dodecene conversion and selectivity to LAB), with decreasing $SiO_2/Al_2O_3$ ratio.

5. The desilication of BEA and MOR zeolites by alkali treatment improved activity and selectivity to 2-phenyldodecane due the enhanced acidity and diffusion behavior in the micro-meso hierarchical structure. The selectivity to dodecene isomers significantly dropped in all desilicated zeolites indicating somewhat lower isomerization activity. Desilicated mordenite ($SiO_2/Al_2O_3$ = 18) exhibited the highest 1-dodecene conversion compared with the other desilicated zeolites. Selectivity to LAB was almost 100%, and the selectivity to 2-LAB was 70% at

99% 1-dodecene conversion. However, the enhancement in the catalytic performance of desilicated BEA was higher than that of desilicated MOR in terms of 1-dodecene conversion and 2-LAB selectivity. This may be attributed to the difference in mesoporosity improvement between the two zeolites.

The kinetics of benzene alkylation with dodecene was studied over mordenite with $SiO_2/Al_2O_3$ = 20 (MOR-20). The major findings of the kinetic study are as follows:

1. Dodecene conversion, yield of linear alkylbenzene isomers and selectivity of the most readily biodegradable isomer (2-phenyldodecane) increase significantly with the increase in temperature (up to 140 °C) and contact time.
2. Kinetic parameters for the dodecene isomerization showed that apparent activation energies for double bond isomerization increased as follows:

$$\mathbf{E_{1\text{-}DD\ -\ 2\text{-}DD} < E_{2\text{-}DD\ -\ 3\text{-}DD}}$$

   Which depicts the faster double bond isomerization of 1-dodecene than the 2-dodecene isomerized to 3-dodecene.
3. For MOR-20, the yield of 2-phenyldodecane is the highest than any other LAB isomer therefore activation energy for alkylation of benzene to 2-phenyldodecane (48.5 kJ/mol) is less than the one for alkylation to 3-phenyldodecane (66 kJ/mol).
4. The double bond isomerization of dodecne follows a ‘reversible path’ whereas alkylation of benzene is ‘irreversible’ i.e., there is no de-alkylation over MOR-20.

# CHAPTER 8

# FUTURE RECOMMENDATIONS

1. Investigation of adsorption kinetics using Langmiur-Hinshlewood type mechanism for Benzene alkylation over MOR-20 should be ventured into to exactly determine the reaction mechanism and intermediate species formed e.g., carbenium ion.

2. Investigate another zeolite based catalyst to see the effect of desilication.

3. Detailed study of catalyst deactivation. This will help in the development of a zeolite based solid acid catalyst with large stability which can be used on commercial scale.

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